VARIATIONAL CALCULATIONS OF THE SPIN-SPIN COUPLING CONSTANT OF HYDROGEN DEUTERIDE

by

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ABSTRACT OF THESIS

There does not exist, at present, any definitive method of calculating nuclear spin-spin coupling constants. The main contribution to nuclear spin-spin coupling between hydrogen atoms is due to what is called "Fermi contact" interaction. Unfortunately the traditional operator used to represent this interaction is valid to only first order in perturbation theory and results in infinite second order self-coupling energies when either perturbation or perturbation-variation methods are applied. Phenomenological operators have been developed which remove the singularities at the nucleus which cause the diverging second order energy.

This thesis summarizes general nuclear spin-spin coupling theory and the derivation of appropriate operators, reviews previous work in this area, and presents a number of variational calculations of the Fermi contact part of the spin-spin coupling constant of hydrogen deuteride, all using a phenomenological operator developed by T.W. Dingle. There were two different approaches to the problem:

1) The first set of calculations used a one-electron approximation which allowed comparison with

previous work reported by other researchers who used a similar operator.

2) The second set of calculations used a more accurate method that allowed for the retention of two-electron interaction terms.

While the one-electron calculations gave good results under specific constraints, the two-electron calculations yielded rather poor results. The trial wave functions used in the latter instance were probably inadequate to describe the effect of spin-spin coupling on the electronic charge distribution in the molecule. A discussion of the criteria which should be used to select such a wave function and some tentative proposals as to the form of the wave function are presented at the end of the thesis.

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CHAPTER 1

INTRODUCTION TO SPIN-SPIN COUPLING CALCULATIONS

1.1 GENERAL THEORY

The magnetic behavior of a nucleus depends upon the interaction of the magnetic moment, associated with its spin angular momentum, with external fields and the electrons and other nuclei in the molecule. As with electronic systems, nuclear angular momentum is expressed in terms of a spin number, I. For any given type of nuclear isotope, I is constant and its value is always some multiple of $\frac{1}{2}$. The largest measurable value of the square of the spin angular momentum is $I(I + 1)\hbar^2$, where $\hbar = h/2\pi$ and $h = 6.626 \times 10^{-34}$ Js is Planck's constant. Its projection along the axis of the main field is quantized, i.e. it will have the value $m_I\hbar$ where m is the magnetic quantum number:

$$m_I = I, I-1, \ldots, -I \tag{1.1}$$

This represents a total of 2I + 1 states.

The magnetic moment of a nucleus is given by:

$$\mu = g_N I \beta_N \tag{1.2}$$

where g_N is the nuclear g factor (also called the Landé or spectroscopic splitting factor) which is a measure of spin motion of the nucleus in relation to its total angular momentum.

is called the nuclear Bohr magneton, which is defined in terms of the hydrogen nucleus:

$$\beta_N = e\hbar/2M_H c \qquad (1.2(a))$$

where M_H is the mass of the hydrogen nucleus

c is the velocity of electromagnetic radiation

e is the charge on one electron.

For a hydrogen nucleus, $g_H = 5.58490$ and $\beta_H = 5.050951 \times 10^{-27}$ J/T.

If I is non-vanishing, the magnetic moment vector is always parallel to the angular momentum vector and has a maximum observable component μ_N:

$$\mu_N = g_N \frac{M_H}{M_N} \beta_N [I(I+1)]^{1/2} \qquad (1.3)$$

Magnetic properties are sometimes expressed in terms of the magnetogyric ratio:

$$\gamma_N = \mu_N / I\hbar \qquad (1.4)$$

For a proton, $\gamma_N = 4.2577 \times 10^7$ Hz/T

In the absence of external magnetic forces, the 2I + 1 states all have the same energy, but upon the application of a magnetic field, $\vec{H}_o$, they split into 2I + 1 equally spaced energy levels. Nuclear magnetic resonance spectra are the results of transitions between these energy levels. Such a system can be described in mathematical

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terms by applying an operator, based on the interaction between an external magnetic field operator and the angular momentum operator $\hat{I}$ that corresponds to the spin number I, to a set of spin functions which represent the 2I + 1 states. The operator which corresponds to the nucleus - magnetic field interaction is:

$$\mathcal{H}_{ns} = -\hat{\mu} \cdot \hat{H}_o \qquad (1.5)$$

where $\hat{H}_o$ is the external magnetic field operator and $\hat{\mu}$ is the magnetic moment operator such that:

$$\hat{\mu} = -\gamma_N \hbar \hat{I} \qquad (1.6)$$

The energy levels are given by:

$$E = \gamma_N \hbar m_I H_o \qquad (1.7)$$

However, in a molecule the energy levels and hence the frequencies of absorption can be affected by two other factors:

(i) Chemical Shift: Nuclei of the same species in different chemical environments absorb energy at different frequencies (ν_N) due to the fact that they are shielded to different extents from the applied magnetic field by the electrons in the molecule. The operator in Eq. (1.5) must then be modified:

$$\mathcal{H}_{ns} = -\hat{\mu} \cdot \hat{H}_o (1 - \sigma_i) \qquad (1.8)$$

where σ_i is the shielding coefficient of the nucleus under consideration.

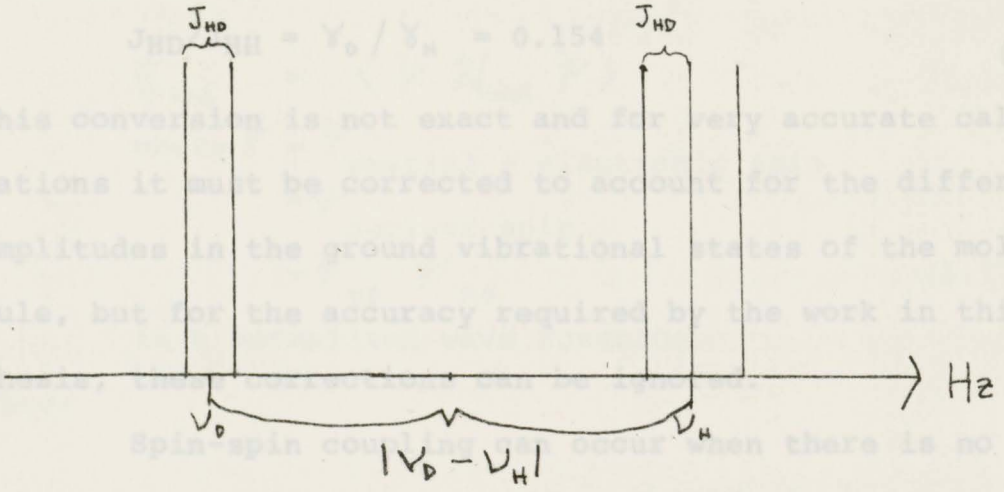
The details of chemical shift are not of concern here and will not be discussed further.

(ii) Spin-spin Coupling

Compounds with nuclei in more than one chemical environment and $I \neq 0$ may exhibit multiplet splitting. This splitting is due to coupling between the nuclear spins and occurs directly through space and also via the bonding electrons. Each energy level can be shifted and this may lead to an increase in the number of lines in the NMR spectrum. The separation of lines due to spin-spin coupling is independent of external field strength and is described in terms of a coupling constant $J_{NN'}$, where N and N' are the two coupled nuclei. In a first order spectrum ($J_{NN'} << \delta_{NN'}$ where $\delta_{NN'} = |\delta_N - \delta_{N'}| = \frac{|\nu_N - \nu_{N'}|}{\nu_{ref}}$ is the difference between chemical shifts), a nucleus surrounded by n indistinguishable nuclei will be split into $2nI + 1$ components, where I is the spin number of the surrounding nuclei. For example, for HD, $I_H = \frac{1}{2}$, $I_D = 1$, and $n = 1$, so that the absorption for the hydrogen is split into three components and the absorption for deuterium is split into two. Thus the spectrum of HD has the qualitative appearance given in Figure 1:

Figure 1

NMR Spectrum of HD



Since each nucleus in this case is coupled to only one other nucleus, all lines in ν_D and in ν_H have equal intensity. For cases in which n > 1, the situation is more complex and the lines within a given splitting can have different intensities.

Spin-spin coupling is not observed between nuclei which are magnetically equivalent, but this does not necessarily mean that there is no coupling between them. It can be proven[1] that the transition energy in such cases is independent of the coupling term so that only a single resonance is observed.

It is possible to obtain a fairly exact estimate of the magnitude of the coupling constant in some cases from known values for the same molecule in which one of the nuclei is replaced by one of its isotopes. For example,

in the case of the hydrogen molecule, J_{HD}/J_{HH} is equal to the ratio of the magnetogyric ratios of the two nuclei:

$$J_{HD}/J_{HH} = \gamma_D / \gamma_H = 0.154 \tag{1.9}$$

This conversion is not exact and for very accurate calculations it must be corrected to account for the different amplitudes in the ground vibrational states of the molecule, but for the accuracy required by the work in this thesis, these corrections can be ignored.

Spin-spin coupling can occur when there is no external magnetic field. Therefore, the operator representing spin-spin coupling must contain terms which depend on the internuclear interaction only. This operator, $\mathcal{H}_{ns}$, can be expressed at two levels of sophistication. The first is a purely phenomenological operator in which the spin-spin coupling constants, $J_{NN'}$, occur as parameters:

$$\mathcal{H}_{ns} = \sum_{N'} \sum_{<N} J_{NN'} (\hat{I}_N \cdot \hat{I}_{N'}) + \sum_N \gamma_N (\hat{H}_o \cdot \hat{I}_N) \tag{1.10}$$

where the first term represents the internuclear interaction and the second term represents the external field - nuclear field interaction.

If the total Hamiltonian is considered, that is, the familiar $\mathcal{H}_o$ representing the electronic interactions is included:

$$\mathcal{H}_{total} = \mathcal{H}_o + \mathcal{H}_{ns} \tag{1.11}$$

then the energy of the system is given by:

$$E_{total} = \langle \psi \mathcal{H}_{total} \psi \rangle \tag{1.12(a)}$$

where $\psi = \psi_{\text{spatial + electronic spin}} \times \psi_{\text{nuclear spin}}$

$$= \psi_{se} \psi_{ns} \tag{1.12(b)}$$

is a normalized wave function.

Thus:

$$E_{total} = \langle \psi_{se} \psi_{ns} | \mathcal{H}_o + \mathcal{H}_{ns} | \psi_{se} \psi_{ns} \rangle$$

$$= \langle \psi_{se} \mathcal{H}_o \psi_{se} \rangle \langle \psi_{ns} \psi_{ns} \rangle + \langle \psi \mathcal{H}_{ns} \psi \rangle$$

$$= E_o + \langle \psi \mathcal{H}_{ns} \psi \rangle \tag{1.13}$$

Substituting Eq. 1.10 into 1.13:

$$E_{total} = E_o + \langle \psi \mathcal{H}_{ns} \psi \rangle$$

$$= E_o + \langle \psi_{se} \psi_{ns} | \sum_{N'<N} \sum_{N} J_{NN'} (\hat{I}_{N'} \cdot \hat{I}_N) + \sum_N \gamma_N (\vec{H} \cdot \hat{I}_N) | \psi_{se} \psi_{ns} \rangle \tag{1.14}$$

This expression gives the possible energy levels for the system when spin-spin coupling is taken into account, and allows for the analysis of the NMR spectrum. However, a quantitative analysis requires a knowledge of the coupling constants $J_{NN'}$.

In a first order situation $\left(J_{NN'} << |\nu_N - \nu_{N'}|\right)$ the

energy associated with spin-spin coupling can be considered independently of the interaction with the applied field. For hydrogen deuteride, the spin-spin coupling operator is given by:

$$\mathcal{H}_{ns} = J_{HH}\,\hat{I}_H \cdot \hat{I}_H + J_{DD}\,\hat{I}_D \cdot \hat{I}_D + J_{HD}\,\hat{I}_H \cdot \hat{I}_D \qquad (1.15)$$

The relationship between the magnetic quantum number ($m_I = \frac{\pm 3}{2}, \frac{\pm 1}{2}$) and the possible wave functions is given in Table 1.

In the presence of a magnetic field, the ground state of the HD molecule will be split by the interaction of the two nuclei with the field; the hydrogen nucleus ($I = \frac{1}{2}$) will yield two separate states and the deuterium nucleus ($I = 1$) will split each of these into three. Spin-spin coupling will further affect the energies of the states. An energy level diagram for such a system is shown in Figure 2.

From Figure 2 it is obvious that there are three possible energy transitions for the H nucleus and two possible energy transitions for the D nucleus:

H		D	
	$\nu_H - J_{HD}$		$\nu_D - J_{HD}$
	ν_H		$\nu_D + J_{HD}$
	$\nu_H + J_{HD}$		

These yield the spectrum given in Figure 1. It should be

Table 1

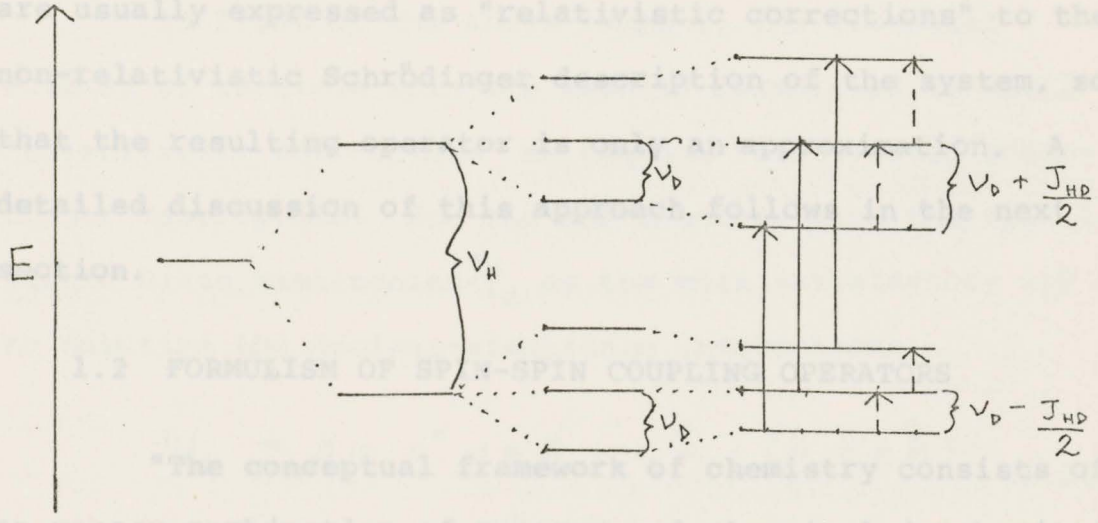
Relationship between M_I
and Nuclear Spin Wave Functions of HD

M_I	Wave Functions	
	Parallel Spins	Antiparallel Spins
$+\frac{3}{2}$	aA	
$+\frac{1}{2}$	a0	bA
$-\frac{1}{2}$	aB	b0
$-\frac{3}{2}$		bB

Lower case letters represent the hydrogen nucleus ($a = \frac{1}{2}$, $b = \frac{1}{2}$). Upper case letters represent the deuterium nucleus ($A = 1$, $0 = 0$, $B = -1$).

Figure 2

Energy Levels of HD
in the Presence of a Magnetic Field



Solid arrows indicate energy transitions which are allowed for the H nucleus. Dashed arrows indicate energy transitions which are allowed for the D nucleus.

noted that for a non-first order case, mixing occurs between states and the position of the energy levels and hence the transitions between them is more complex than depicted in Figure 2.

A more sophisticated approach is to try to develop an operator which expresses the $J_{NN'}$ in terms of the interaction between the magnetic effects due to the nuclear spins and those associated with the spin and orbital motion of the electrons. Since particle spin is essentially a relativistic effect, the nuclear spin operator should, in theory, be derived from relativistic considerations of the electromagnetic interactions. However, relativistic calculations are difficult for one and two particle systems and impossible for many particle systems. The effects of spin are usually expressed as "relativistic corrections" to the non-relativistic Schrödinger description of the system, so that the resulting operator is only an approximation. A detailed discussion of this approach follows in the next section.

1.2 FORMULISM OF SPIN-SPIN COUPLING OPERATORS

"The conceptual framework of chemistry consists of an uneasy combination of quantum and classical (mechanistic) ideas. When one comes to consider the possibility of a theory of spin interactions in molecules one must take

cognizance of the radically different interpretation of the quantum uncertainty relations which is forced by the existance of a limiting velocity (the velocity of light). This leads to the conclusion that particle co-ordinates and momenta *cannot* act as dynamical variables since they have no precise significance in a relativistic theory and so the entire formalism of non-relativistic quantum mechanics predicted on the probablistic interpretation of the wave function must be given up if one is to achieve a consistent relativistic theory. Consequently one cannot give a precise meaning to the idea of spin-spin coupling within a molecule, and if one insists on retaining the idea the most one can hope to achieve is a non-relativistic phenomenology."[49]

In light of the above comment, the essential effects of particle spin are usually formulated as small "relativistic corrections" to the non-relativistic Schrodinger description. For the one-electron atom the relativistic Dirac Hamiltonian $\mathcal{H}_D$ as the most satisfactory way to describe the nuclear-electronic interactions:

$$\mathcal{H}_D = \beta m_e c^2 - e\phi + c\hat{\alpha} \cdot (\hat{p} + e\hat{A}) \qquad (1.16)$$

where m_e, $-e$, and $\hat{p}$ are the mass, charge, and canonical momentum of the electron, respectively $\hat{\alpha}$ and β are the Dirac operators, usually

represented by 4 x 4 matrices so that the wave functions associated with the Dirac Equation have four components (two corresponding roughly to positive energy and two corresponding to negative energy) and are called spinors.

The electronic potential ϕ and the magnetic potential $\hat{A}$ are given by Eq. (1.17) and (1.18):

$$\phi = ze/4\pi\epsilon_0 r \qquad (1.17)$$

$$\hat{A} = (g_N \mu_N / 4\pi\epsilon_0 c^2)\hat{I} \wedge \hat{r}/\hat{r}^3 \qquad (1.18)$$

The Dirac formulism ignores radiative effects (which may be introduced phenomenologically if necessary) and approximates the nucleus by a point charge.

There are a number of methods used to reduce the Dirac Equation to a non-relativistic form:

(i) a partitioning technique known as "the method of large and small components"[55]

(ii) a unitary transformation utilizing a series expansion (the Foldy and Wouthuysen method)[56]

(iii) the projection technique of Feynmann and Gell-man.[57]

In all cases the resulting Hamiltonian is an infinite series in powers of an appropriate parameter. The higher order terms result from the elimination of coupling between the four components of the spinors.

For calculation of second order hyperfine energies the relevant terms are:

$$\hat{\mathcal{H}}_D = mc^2 + \hat{p}^2/2m - e\phi \qquad (1.19(a))$$

$$+ (e/m)\hat{A}\cdot\hat{p} \qquad (1.19(b))$$

$$+ (e\hbar/m)\hat{s}\cdot\hat{\nabla}\wedge\hat{A} \qquad (1.19(c))$$

$$+ (e^2/2m)A^2 \qquad (1.19(d))$$

$$+ (ie^2/m)\hat{s}\cdot\hat{A}\wedge\hat{A} \qquad (1.19(e))$$

$$+ \ldots \text{ higher order terms}$$

Eq. (1.19(a)) corresponds to the zeroth-order one-electron Hamiltonian. Substituting Eq. (1.18) into (1.19(b)) results in a term proportional to $\hat{I}\cdot\hat{1}$, which goes to zero when only s states are under consideration and does not contribute to second order energies. The perturbation 1.19(c), which involves the magnetic field due to the nuclear magnetic moment, yields both the dipole-dipole interaction operator (Eq. 1.20) and the Fermi contact term (Eq. 1.21):

$$-(g g_N \mu_B \mu_N/4\pi\epsilon_0 c^2) \times [(\hat{s}\cdot\hat{I})/r^3 - 3(\hat{s}\cdot\hat{r})(\hat{I}\cdot\hat{r})/r^5] \qquad (1.20)$$

$$(2g g_N \mu_B \mu_N/3\epsilon_0 c^2)\,\delta(\hat{r})\,(\hat{s}\cdot\hat{I}) \qquad (1.21)$$

Equations 1.19(d) and 1.19(e) compensate for the removal of the contribution from relativistic negative energy states to the second order perturbation energy.[50]

Mathematical representation for systems with more than one electron cannot be formulated exactly. Such systems include an interaction term between the two electrons. The usual method of treating a two-body system is to assume that the operator may be expressed as:

$$\mathcal{H} = \mathcal{H}_1' + \mathcal{H}_2' + \text{interaction term where} \qquad (1.22)$$

$\mathcal{H}_1'$ and $\mathcal{H}_2'$ are Dirac operators reduced to the expanded form of 1.19 and the interaction term is derived by considering each electron separately and assuming the other electron is a source of electrical and magnetic fields. For a two-electron system, the Breit Equation (1.23) is analogous to the one-electron Dirac Equation:

$$\mathcal{H}_B = \mathcal{H}_1' + \mathcal{H}_2' \qquad (1.23(a))$$

$$+ \; e_1 e_2 / 4\pi\epsilon_0 r_{12} \qquad (1.23(b))$$

$$- \frac{e_1 e_2}{8\pi\epsilon_0 m_1 m_2 e^2} \left[\hat{\Pi}_1 \left(\frac{\hat{\Pi}_2}{r_{12}} \right) + \left(\hat{\Pi}_1 \cdot \hat{r}_{12} \right) \frac{1}{r_{12}^3} \left(\hat{\Pi}_2 \cdot \hat{r}_{12} \right) \right] \qquad (1.23(c))$$

$$- \frac{e_1 e_2}{8\pi\epsilon_0 c^2 r_{12}} \left[\frac{\hat{s}_1 \cdot (\hat{r}_{12} \wedge \hat{\pi}_1)}{m_1^2} - \frac{\hat{s}_2 \cdot (\hat{r}_{12} \wedge \hat{\pi}_2)}{m_2^2} \right] \quad (1.23(d))$$

$$+ \frac{e_1 e_2 \hbar}{4\pi\epsilon_0 m_1 m_2 c^3 r_{12}^3} \times \left[\hat{s}_1 \cdot (\hat{r}_{12} \wedge \hat{\pi}_2) - \hat{s}_2 \cdot (\hat{r}_{12} \wedge \hat{\pi}_1) \right] \quad (1.23(e))$$

$$+ \frac{e_1 e_2 \hbar^2}{4\pi\epsilon_0 / 4\pi\epsilon_0 m_1 m_2 c^2} \times \left[\frac{\hat{s}_1 \hat{s}_2}{r_{12}^3} - \frac{3(\hat{s}_1 \cdot \hat{r}_{12})(\hat{s}_2 \cdot \hat{r}_{12})}{r_{12}^5} - \frac{8\pi}{3} \delta(\hat{r}_{12}) (\hat{s}_1 \cdot \hat{s}_2) \right] \quad (1.23(f))$$

+ ... higher order terms

where $\hat{\pi}_i = \hat{p}_i + e\hat{A}_i$ (1.24)

Equation 1.23(b) is the normal zeroth-order electrostatic repulsion term. The term in Eq. 1.23(c) represents orbit-orbit coupling while Eq. 1.23(d) and Eq. 1.23(e) represent spin-orbit coupling. Eq. 1.23(f) represents spin-spin coupling and is analogous to Eq. 1.20 and 1.21 combined.

The Dirac theory correctly predicts the nuclear g-factor (g_N) but fails to predict the anomalous magnetic

moments that are obtained experimentally. These magnetic moments may be included phenomenologically provided that no terms characteristic of the Dirac theory remain in the non-relativistic formulism. In effect this limits the use of the Breit Equation in perturbation theory to first order and some but not all second order phenomena.

In order to calculate spin-spin coupling constants, Eq. 1.23 must be extended to molecules:

$$\mathcal{H} = \sum_i \left(\frac{\hat{\pi}_i^2}{2m} - e\phi_i \right) + g_N \beta_N \left(\hat{s}_i \cdot \beta_i \right)$$

$$- \frac{g_N \beta_N}{2mc^2} \hat{s}_i \left[\hat{\pi}_i \wedge E_i - E_i \wedge \hat{\pi}_i \right]$$

+ electron repulsion terms
+ electron spin - electron spin interaction terms
+ smaller relativistic terms
+ purely nuclear terms such as nuclear kinetic energy and electrostatic terms
+ nuclear spin magnetic interaction (1.25)

where

$$\hat{\pi}_i = \hat{p}_i + e\hat{A}_i$$

$$= \hat{p}_i + \frac{e}{c} \sum_N \gamma_N \frac{\left(\hat{I}_N \wedge \hat{r}_{iN} \right)}{r_{iN}^3} \qquad (1.26)$$

The terms in Eq. 1.25 for which no formulae are given are unimportant in this work and can be ignored. Substitution of Eq. 1.26 into Eq. 1.25 and expansion leads to an operator which is often partitioned into five sub-operators:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{1ns} + \mathcal{H}_{2ns} + \mathcal{H}_{3ns} + \mathcal{H}_{4ns} \qquad (1.27)$$

where $\mathcal{H}_0$ is the usual electronic operator with no nuclear spin terms

$$\mathcal{H}_{1ns} = \frac{e}{mc} \sum_i \sum_N \frac{\gamma_N \hat{I}_N \cdot \hat{r}_N \wedge \hat{p}_i}{r_{iN}^3}$$

$$= \frac{e}{mc} \sum_i \sum_N \frac{\gamma_N \hat{I}_N \cdot \hat{\ell}_i}{r_{iN}^3} \qquad (1.27(a))$$

$$\mathcal{H}_{2ns} = g_N \beta_N \sum_i \sum_N \gamma_N \left[-\frac{\hat{S}_i \cdot \hat{I}_N}{r_{iN}^3} + \frac{3(\hat{I}_N \cdot \hat{r}_{iN})(\hat{S}_i \cdot \hat{r}_{iN})}{r_{iN}^5} \right] \qquad (1.27(b))$$

$$\mathcal{H}_{3ns} = -\frac{8\pi}{3} \sum_i \sum_N (\hat{S}_i \cdot \hat{I}_N)\, \delta(\hat{r}_{iN}) \qquad (1.27(c))$$

$$\mathcal{H}_{4ns} = \frac{e^2}{2mc^2} \sum_i \sum_N \sum_{N'} \frac{\gamma_N \gamma_{N'}}{r_{iN}^3\, r_{iN'}^3} \times \left[(\hat{I}_N \cdot \hat{I}_{N'})(\hat{r}_{iN} \cdot \hat{r}_{iN'}) - (\hat{I}_N \cdot r_{iN'})(\hat{I}_{N'} \cdot \hat{r}_{iN}) \right] \qquad (1.27(d))$$

Since there is no external magnetic field in the system considered here, the magnetic interactions represented by $\mathcal{H}_{ns}$ in Eq. 1.27 are restricted to intramolecular and intermolecular effects. Electron orbital-orbital, orbital-spin, and spin-spin interactions have been ignored because these are negligible for singlet molecular states. The operator $\mathcal{H}_{1ns}$ consists of magnetic shielding terms. In both 1.27(b) and 1.27(c) the operators describe nucleus-electron-electron-nucleus spin interaction. $\mathcal{H}_{3ns}$, which according to Ramsey[3] represents the interaction of the nuclear spins through magnetic polarization of nearby electrons, is referred to as the Fermi contact operator. $\mathcal{H}_{4ns}$ represents direct nuclear dipole-dipole interaction.

For fluids in which all molecular orientations are equally probable, $\mathcal{H}_{4ns}$ averages to zero.

1.3 PERTURBATION CALCULATIONS

The operator given by Eq. 1.27 is the starting point for most calculations of spin-spin coupling, although simplifications are sometimes made. The first and most commonly used non-relativistic nuclear spin operator was derived by Ramsey[2,3]. The nuclear interaction energy $E_{NN'}$ for two nuclei N and N' in a molecule with a specific orientation λ may be written as:

$$E_{NN'} = h\hat{I}_N \cdot \mathbb{J}_{NN'} \cdot \hat{I}_{N'} + hJ_{NN'} \cdot \hat{I}_N \cdot \hat{I}_{N'} \qquad (1.28(a))$$

where $\mathbb{J}_{NN'}$ is a tensor.

If there are frequent intermolecular collisions (as in the liquid state), $\mathbb{J}$ averages to zero.

$$(E_{NN'})_{avg} = hJ_{NN'}\hat{I}_N \cdot \hat{I}_{N'} \qquad (1.28(b))$$

The operator in Eq. 1.27 contains both self-coupling and cross-coupling terms. Ramsey calculated the cross-term energy by selecting only those parts of the operator which depend upon both $\hat{I}_N$ and $\hat{I}_{N'}$. Since the nuclear spin contribution to the total molecular energy is small, Ramsey and others using his approach decided to use the

perturbation method (cf Appendix 1). A perturbation calculation to the second order gives the energy:

$$\sum_{N \neq N'} E_{NN'} = \sum \frac{1}{E_n - E_0} \langle 0 | \mathcal{H}_{ns} | n \rangle \langle n | \mathcal{H}_{ns} | 0 \rangle \tag{1.29}$$

Thus the contributions to the coupling constant represented by $\mathcal{H}_{1ns}$, $\mathcal{H}_{2ns}$, and $\mathcal{H}_{3ns}$ are given by:

$$J_{1NN'} = \frac{\pi}{3} \gamma_N \gamma_{N'} \left\{ \frac{1}{h} \left\langle 0 \left| \frac{e^2 \hbar^2}{2 m_k c^2} \frac{\hat{r}_{kN'} \cdot \hat{r}_{kN}}{r_{kN'}^3 \, r_{kN}^3} \right| n \right\rangle \right.$$

$$\left. - 2\hbar^2 \sum_{nkj} \left[\frac{1}{E_n - E_0} \right] \left\langle 0 \left| \frac{\hat{m}^0_{kN}}{r^3_{kN}} \right| n \right\rangle \left\langle n \left| \frac{\hat{m}^0_{jN'}}{r^3_{jN'}} \right| 0 \right\rangle \right\} \tag{1.30(a)}$$

$$J_{2NN'} = -\frac{2}{3} (2\beta\hbar)^2 \gamma_N \gamma_{N'} \sum_{njk} \left[\frac{1}{E_n - E_0} \right]$$

$$\times \left\langle 0 \left| \left\{ \frac{3(\hat{S}_k \cdot \hat{r}_{kN}) \cdot \hat{r}_{kN}}{r^5_{kN}} - \frac{\hat{S}_k}{r^3_{kN}} \right\} \right| n \right\rangle$$

$$\times \left\langle n \left| \left\{ \frac{3(\hat{S}_j \cdot \hat{r}_{jN'}) \cdot \hat{r}_{jN'}}{r^5_{jN'}} - \frac{\hat{S}_j}{r^3_{jN'}} \right| 0 \right\rangle \right. \tag{1.30(b)}$$

$$J_{3NN'} = \left(-\frac{2}{3h} \right) \left(\frac{16\pi\beta\hbar}{3} \right)^2 \gamma_N \gamma_{N'} \sum_{njk} \left[\frac{1}{E_n - E_0} \right]$$

$$\times \langle 0 | \delta(\hat{r}_{kN}) \cdot \hat{S}_k | n \rangle \langle n | \delta(\hat{r}_{jN'}) \cdot \hat{S}_j | 0 \rangle \tag{1.30(c)}$$

Evaluation of the summations in Eq. 1.29 and 1.30 is in practice impossible because it requires a knowledge of all of the exact excited state wave functions. Ramsey and other early researchers[4,5,6,7] approximated these expressions using the average energy approximation (AEA). Using this method, Eq. 1.29 reduces to:

$$\sum_{N \neq N'} E_{NN'} = \frac{1}{\Delta E} \langle 0 | \mathcal{H}_{ns}^2 | 0 \rangle \qquad (1.31)$$

where ΔE is determined semi-empirically, Ramsey used the AEA approach to calculate the contributions of J_{1HD}, J_{2HD}, and J_{3HD} to the coupling constant of HD.[3] He discovered that J_{3HD} contributed about 40 Hz out of the total of ∿43Hz. Since the Fermi contact term accounts for most of the nuclear coupling via the electrons in H_2 and HD, many calculations of the coupling constants of these molecules omit the contribution from other terms entirely.

The main problem of the AEA method is that it requires some systematic scheme to determine ΔE, if the method is to be applied routinely to a large number of molecules. Since the summation over excited states depends upon the electron density at the nucleus, which falls off rapidly for states with increasing energy, later researchers proposed calculating the lower level states and truncating after a few terms.[7,8,9] Unfortunately, this tends to lead to convergence problems and the results

are not consistently accurate. The excited state wave functions for this "sum of states" (SOS) method are commonly constructed using ground state virtual orbitals as a basis[8,9], but this approximation can lead to errors because the results tend to be highly dependent on the form of the wave function.[7,8,9,10,11]

Both valence bond and molecular orbital wave functions have been used as bases for AEA and SOS calculations, with varying results. In general, MO calculations tend to be low and predict a positive sign even for molecules with a negative coupling constant. This latter error is due to the absence of electron correlation in the mathematical representation. (Since the major contribution to spin-spin coupling occurs via the electrons, electron correlation can have a large effect.) Attempts to include correlation by introducing configuration interaction into the wave function for the HD molecule have had a variety of success.[7,8,9,11,12,13] Ditchfield et al[7] and Kirtman et al[13] obtained good results (J_{HD} = 40Hz and 40.5 Hz respectively), but only at the expense of a large amount of computation. Correlation effects can also be introduced via a perturbation operator.[14,15,16,17,18] Although good results are also possible using this method,[16,18] the computations involved are, again, extensive. For larger molecules the combined calculation of both the excited

states and correlation effects would be prohibitive.

Even if the computational difficulties can be overcome or discounted, the validity of the AEA and SOS methods is doubtful. The preceding calculations have considered only the cross term energy rather than the entire second order energy:

$$E^{(2)} = E_{NN} + E_{N'N'} + E_{NN'} \qquad (1.32)$$

Unfortunately the self-coupling contributions E_{NN} and $E_{NN'}$ due to the Fermi contact term are infinite. The exact first order wave function calculated by Schwartz[19] for second order perturbations in the hydrogen atom contains singularities which result in infinite self-coupling terms when operated on by the delta function (see discussion in Section 1.4). This is because the delta function is valid only to first order in perturbation theory.

Since the Fermi contact term contributes the largest part of the spin-spin coupling energy in H_2 and HD, it can hardly be neglected, so in order to preserve physical sense the self-coupling energies are assumed to cancel so that:

$$E^{(2)} = E_{NN'} \qquad (1.32(a))$$

However, this has never been proven and is probably not a valid assumption. A less stringent assumption is to

assume that the transition energy, which is related to the coupling constant, depends only upon the difference between the cross-coupling energies:

$$\Delta E^{(2)} = \Delta E_{NN} + \Delta E_{N'N'} + \Delta E_{NN'} = \Delta E_{NN'} \qquad (1.32(b))$$

i.e. the self coupling energies are the same in both energy levels and the transition energy is equal to the differences between the cross-coupling energies in the two levels.

One method that has been proposed to avoid both the difficulties of the excited state expansion and the problems caused by the limitations of the delta function in calculating second order energies is the finite perturbation method. This method expresses the second order energy as a Taylor expansion:

$$\tfrac{1}{2} E_{rs} = \left\langle \psi^{(0)} \mathcal{H}'_r \left[\frac{\partial \psi(\lambda)}{\partial \lambda_s} \right]_{\lambda=0} \right\rangle$$

$$= \left[\frac{\partial f_r(\lambda)}{\partial \lambda_s} \right]_{\lambda=0} \qquad (1.33)$$

where the expectation value of $f_r(\lambda)$ in LCAO-MO theory is dependent on the first order density matrix $\rho_{\mu\nu}(\lambda)$:

$$\rho_{\mu\nu}(\lambda) = \sum_{i}^{occ} C_{\mu i} C_{\nu i} \qquad (1.34)$$

The method allows the calculation of $J_{NN'}$ between nucleus N and any other nucleus N' by introducing an artificially large nuclear moment centered on N directly into a

self-consistent field (SCF) wave function and calculating the effect of the perturbation on the second nucleus as the size of the perturbation interaction goes to zero. Since the perturbation causes an uneven distribution of α and β electrons, the perturbed wave function must be calculated in an unrestricted formulism. The spin density matrix can then be defined as:

$$\rho_{\mu\nu}(\lambda) = P^{\alpha}_{\mu\nu}(\lambda) - P^{\beta}_{\mu\nu}(\lambda) \tag{1.35}$$

where $P^{\alpha}_{\mu\nu}(\lambda)$ is the first order density matrix for α spin and $P^{\beta}_{\mu\nu}(\lambda)$ is the corresponding matrix for β spin

so that the calculation of the coupling constant $J_{NN'}$ involves derivatives of the form $\left[\frac{\partial \rho_{\mu\nu}(\lambda)}{\partial \lambda}\right]_{\lambda=0}$. For any basis set ϕ_μ the expression for the coupling constant is given by:

$$J_{NN'} = \frac{2h}{3\pi} \gamma_N \gamma_{N'} \beta_N \sum_{\mu,\nu} \phi_\mu \delta(r_{N'}) \phi_\nu \, d\tau \times \left[\frac{\partial \rho_{\mu\nu}(\mu_N)}{\partial \mu_N}\right]_{\mu_N} \tag{1.36(a)}$$

The FP method was introduced by Pople et al[20] who applied it to a number of different molecules (including H_2) using INDO (approximate) wave functions. Under this approximation, the integral in Eq. 1.36(a) becomes:

$$\int \phi_\mu \delta(r_{N'}) \phi_\nu \, d\tau = S_{N'}^2(0) \tag{1.37}$$

where $S_{N'}^2(0)$, the density at the nucleus of the valence s orbital of atom N', is evaluated semi-empirically.

The expression for $J_{NN'}$ after implementing the perturbation then becomes:

$$J_{NN'} = \frac{16 h \gamma_N \gamma_{N'} \beta^2}{9} S_N^2(0) S_{N'}^2(0) \times \left[\frac{\partial \rho_{S_N, S_{N'}}(h_N)}{\partial h_N} \right]_{h_N=0} \tag{1.36(b)}$$

where $h_N = \frac{8\pi}{3} \beta \mu_N S_N^2(0)$ (1.38)

Since $\rho_{S_N, S_{N'}}(h_N)$ is an odd function of h and small in magnitude, only one value of h_N need be used to calculate the wave function. The coupling constant is then approximated by:

$$J_{NN'} = \frac{16 h \gamma_N \gamma_{N'} \beta^2}{9} S_N^2(0) S_{N'}^2(0) \times \left[\frac{\rho_{S_N, S_{N'}}(h_N)}{h_N} \right] \tag{1.36(c)}$$

In a later calculation, Pople et al[21] used a more accurate STO basis. Other FP calculations of J_{H_2} or J_{HD} were performed by Chuvylken and Zhidamov[22] using INDO wave functions and Ditchfield et al[23] using an extended

STO basis. In general, results were variable and for H_2 they were poor (very high). Chuvylken and Zhidamov suggested that results might be improved by determining the $S_N(0)$ functions variationally rather than empirically. However, calculations by Fukio and Hiroyuki,[24] using this method did not give better results. Kirtman[63] reported a similar calculation using a coupled valence bond perturbation method, which is a modification of the finite perturbation approach. His results (J_{3HD} = 43Hz) show promise, but the method is relatively new and still in the process of refinement.

1.4 VARIATIONAL METHODS

Calculations of J_{HD} using the variational method were first proposed as a means of avoiding the arduous computation required by the SOS approach. The earliest such calculation was done by Stephen.[25] Like Ramsey in his perturbation derivations, Stephen broke his operator into parts:

$$\mathcal{H}_{nsi} = I_{N\alpha}\mathcal{H}_\alpha^{(1)} + I_{N'\alpha}\mathcal{H}_\alpha^{(2)} + I_{N\alpha}I_{N'\beta}\mathcal{H}_\alpha^{(3)} \qquad (1.39(a))$$

$$\mathcal{H}_{ns2} + \mathcal{H}_{ns3} = I_{N\alpha}\mathcal{H}_{\alpha}^{(4)} + I_{N'\alpha}\mathcal{H}_{\alpha}^{(5)} + I_{N\alpha}\mathcal{H}_{\alpha}^{(6)} + I_{N'\alpha}\mathcal{H}_{\alpha}^{(7)} \quad (1.39(b))$$

where the α denote tensors

$\mathcal{H}_{ns1}$ includes contributions from the magnetic shielding and electronic orbital interactions, while $\mathcal{H}_{ns2}$ and $\mathcal{H}_{ns3}$ represent contributions from nucleus-electron spin angular momentum. Stephen calculated the coupling constants $J_{\alpha\beta}^{(1)}$ and $J_{\alpha\beta}^{(2)}$ due to the two parts separately, choosing wave functions corresponding to each part:

$$\Psi = \Psi_0 \left(1 + I_{N\alpha} f_{\alpha}^{(N)} + I_{N'\alpha} f_{\alpha}^{(N')}\right) \quad (1.40(a))$$

$$\Psi = \Psi_0 \left(\varphi_s + \varphi_r \left[I_{N\alpha} p_{\alpha}^{(N)} + I_{N'\alpha} p_{\alpha}^{(N')}\right]\right) \quad (1.40(b))$$

where φ_s is an antisymmetric spin function and

φ_r is a symmetric triplet spin function.

The unknown functions f_α and p_α are found by minimizing the energies:

$$E_{NN'}^{(1)} = h J_{\alpha\beta}^{(1)} I_{N\alpha} I_{N'\alpha} \quad (1.41(a))$$

$$E_{NN'}^{(2)} = h J_{\alpha\beta}^{(2)} I_{N\alpha} I_{N'\alpha} \quad (1.41(b))$$

where $E_{NN'} = E_{NN'}^{(1)} + E_{NN'}^{(2)}$ (1.42)

O'Reilly[26] performed similar calculations of J_{2HD} and J_{3HD} only, since the major contribution to the coupling constant seemed to come from these parts. He found that the results were highly dependent on the form of the zeroth order wave function (ψ_0) used to generate the total wave function (ψ).

Later variational calculations were performed using perturbation variation theory. The first order perturbation equation:

$$(\mathcal{H}_0 - E^{(0)})\psi^{(1)} + (\mathcal{H}' - E^{(1)})\psi^{(0)} = 0 \quad (1.43)$$

can be proven[27] equivalent to the variation principle:

$$\tilde{\mathcal{E}}^{(2)} \geq \mathcal{E}^{(2)} \quad (1.44)$$

where $\tilde{\mathcal{E}}^{(2)} = \langle \tilde{\psi}^{(1)} | \mathcal{H}_0 - E_0 | \tilde{\psi}^{(1)} \rangle + \langle \tilde{\psi}^{(1)} | \mathcal{H}' | \psi^{(0)} \rangle + \langle \psi^{(0)} | \mathcal{H}' | \tilde{\psi}^{(1)} \rangle$ (1.45)

where $\psi^{(0)}$ is the exact zero order wave function and $\tilde{\psi}^{(1)}$ is a trial variational wave function.

The equality in Eq. 1.27 is true only when the variation function $\tilde{\psi}^{(1)} = \psi^{(1)}$, the true first order wave function. However, even if the first order equations cannot be solved analytically, it may be possible to obtain a good approximation to $\mathcal{E}^{(2)}$ and $\psi^{(1)}$ by inserting a trial

function $\tilde{\psi}^{(1)}$ in Eq. 1.45 and making $\tilde{\mathcal{E}}^{(2)}$ stationary with respect to the variational parameters contained in $\tilde{\psi}^{(1)}$. This principle was first formulated by Hylleraas[28] and also first employed by him in calculating second order energies.[29] A more detailed discussion of the theory is presented in Appendix 1.

The spin-spin coupling operator in the perturbation variation method is usually chosen to describe a double perturbation:

$$\mathcal{H}_{3ns} = \mu \mathcal{H}_{10} + \nu \mathcal{H}_{01} \tag{1.46}$$

where $\mu = \frac{4\beta^2 h}{3} \gamma_N I_{Nz}$ (1.46(a))

$$\nu = 4\beta^2 h \gamma_{N'} I_{N'z} \tag{1.46(b)}$$

$$\mathcal{H}_{10} = \sum_i 4\pi \delta(\hat{r}_{iN}) S_{iz} \tag{1.46(c)}$$

$$\mathcal{H}_{01} = \sum_i 4\pi \delta(\hat{r}_{iN'}) S_{iz} \tag{1.46(d)}$$

In Equation 1.46 the contact perturbation is assumed to be isotropic so that the nuclear spins can be quantized in the z direction. The corresponding trial function is formulated as a similar expansion:

$$\tilde{\psi}^{(1)} = \mu \tilde{\psi}_{10} + \nu \tilde{\psi}_{01} \tag{1.47}$$

The cross term $E_{NN'}$ can be derived from Eq. 1.45 (see Appendix 1):

$$E_{NN'} = 2\langle \tilde{\psi}_{10} | \mathcal{H}_{01} | \tilde{\psi}_{00} \rangle + 2\langle \psi_{01} | \mathcal{H}_{10} | \psi_{00} \rangle + 2\langle \tilde{\psi}_{10} | \mathcal{H}_0 - E_0 | \tilde{\psi}_{01} \rangle \tag{1.48}$$

Since $E_{NN'}$ is a cross product the sign is ambiguous; hence there is no minimization principle for $E_{NN'}$, and it can at best be made stationary:

$$\frac{\partial E_{NN'}}{\partial \mu} = \frac{\partial E_{NN'}}{\partial \nu} = 0 \tag{1.49}$$

Calculations of J_{HD} using Eq. 1.48 have not been very successful.[30,31,32,33,38] Convergence tends to be poor as the size of the basis set is increased systematically, and results using molecular orbitals in the basis set are usually low (this is characteristic of perturbation calculations using MO bases as well).

The total second order energy consists of the cross-coupling and self-coupling energies combined:

$$E^{(2)} = \mu^2 E_{20} + \nu^2 E_{02} + \mu\nu E_{11}$$

$$= E_{NN} + E_{N'N'} + E_{NN'} \tag{1.50}$$

Both the total and self-coupling energies can be minimized; e.g., for the self-coupling energy E_{NN}:

$$\frac{\partial^2 E_{NN}}{\partial^2 \mu} \geq 0 \qquad (1.51)$$

Unfortunately the Fermi contact part of the self-coupling energies (E_{3NN}) becomes infinite just as it does in perturbation theory. Some researchers have tried to counteract this effect by modifying the trial wave function so that it does not yield singularities under the Dirac delta function.[34,35,36,37,38,39,40] Although most of these calculations do give reasonable results for particular wave functions, they tend to display convergence problems when the size of the basis set is increased systematically.

The Fermi contact operator is successful for first order energy calculations in the H atom, suggesting that the main effect is to sample the electron density at the nucleus. Since p and higher states have zero density at the nucleus, it is common to work with s orbitals only in these calculations. The $\mathcal{H}_{1ns}$ and $\mathcal{H}_{2ns}$ operators contain dipolar terms and integrate to zero energy when only s orbitals are considered. Thus the Fermi contact term accounts for the total hyperfine splitting energy in the H atom under these conditions. For the H atom:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{3ns} \qquad (1.52)$$

where $\mathcal{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r}$ (1.52(a))

$$\mathcal{H}_{3ns} = Q_H \, V(r) \, (\hat{S} \cdot \hat{I}) \qquad (1.52(b))$$

where $$Q_H = \frac{8\pi}{3} g_H \beta_H g_e \beta_e \qquad (1.52(c))$$

$$V(r) = \delta(\hat{r}) = \delta(r)(4\pi r^2)^{-1} \qquad (1.52(d))$$

However, the Dirac delta function results in singularities in the first order wave function because it assumes a point dipole for the nucleus. Schwartz[19] calculated an exact first order wave function for the H atom by solving Eq. A1.8(b) (see Appendix 1):

$$(\mathcal{H}_0 - E^{(0)})\psi^{(1)} + (\mathcal{H}' - E^{(1)})\psi^{(0)} = 0 \qquad A1.8(b)$$

where in this case $\mathcal{H}' = \mathcal{H}_{3ns}$

For the 1s state perturbed by the Fermi contact operator he obtained the wave function:

$$\rho_1^{1s}(r) = \left[\left(\frac{-2}{r}\right) + 2 - \ln r + 2r + C_{1s}\right]\rho_0^{1s}(r) \qquad (1.53)$$

The r^{-1} and ln r terms are singular at r = 0 and are responsible for the infinite self-coupling terms, E_{3NN} and $E_{3N'N'}$ obtained in spin-spin coupling calculations.

It seems reasonable to replace the delta function by an operator which describes nuclear size. One such modification which has been suggested is the Blinder operator:

$$V(r) = B(r, r_o) = (2\pi r^2)^{-1} r_o (r + r_o)^{-2}$$
$$= r^{-2} k'(r, r_o) \qquad (1.54)$$

where $r_o = ze/2mc^2$

$$\simeq 2.7 \times 10^{-5}\ a_o \qquad (1.54(a))$$

where a_o is the atomic radius of hydrogen (Bohr radius)

This operator was originally developed as part of an alternate derivation of the Fermi contact operator from the Dirac equation, but it has a weaker singularity at the origin than the delta function. Power and Pitzer[43,44] replaced the Fermi contact operator in Schwartz' calculations with the Blinder operator and obtained the following result for φ_1^{1s}:

$$\varphi_1^{1s}(r) = \left\{ \frac{1}{2r_o} \ln\frac{(r+r_o)}{r} + \left[\ln(2\gamma(r+r_o)) + \frac{r_o}{r} \ln\frac{(r+r_o)}{r_o} \right] + r + C_{1s} + \text{negligible terms} \right\} \varphi_o^{1s}(r) \qquad (1.55)$$

Examining the equation in the limit as $r \to 0$ reveals the $\ln\frac{(r+r_o)}{r}$ term as the source of the weak singularity. If the operator in Eq. 1.54 is used to calculate the

self-coupling energies, the results are finite. Gregson, Hall, and Rees [42] suggested that the Blinder operator could be replaced by the approximation:

$$V(r) = G(r, r_o) = (4\pi r^2)^{-1} r_o^{-1} \exp\left(\frac{-r}{r_o}\right) \qquad (1.56)$$

Both operators have been used in calculations of J_{HD}. Power and Pitzer[43,44] used the Blinder operator and obtained rapid convergence but a rather high result (53Hz). On the other hand, Paviot and Hoarau[45,46] used the Gregson, Hall, and Rees operator and found convergence (when the size of the basis set was increased systematically) was slow. The Blinder and GHR operators succeed to some extent because they incorporate the idea of finite nuclear size. This is achieved by imposing a non-relativistic cutoff near $r = 0$ via the constant r_o, which approximates the radius of the hydrogen atom nucleus. Unfortunately this parameter has no counterpart in the relativistic results (i.e., the relativistic calculation of hyperfine splitting in the hydrogen atom) and Woolley[49] and Moore and Moss[50] criticize the operators on this ground. If this approach is used, the operator should be significant not only in the region of $r \sim 0$, but it should also be sufficiently smooth so that the self-adjoint property of the Hamiltonian is preserved.

A non-relativistic phenomenological approach to

the effects of nuclear size was developed simultaneously by Dingle[49,51] and Sänger and Voitlander.[52,53] The perturbation operator used in both cases had the form:

$$\mathcal{H}_{nS3} = Q_N V_1(r) \hat{I} \cdot \hat{S} \qquad (1.57)$$

where $Q_N = \frac{8\pi}{3} g_N \beta_N g_e \beta_e$ (1.57(a))

and $V_1(r) = K^3 \exp(-Kr)/8\pi$ (1.57(b))

K is a parameter such that $\frac{1}{K}$ has the dimensions of length (typically $K^{-1} \sim 10^{-5}$ a.u.)

Dingle also used a modified form of this operator in which $V_1(r)$ was replaced by $V_2(r)$:

$$V_2(r) = K^2 \exp(-Kr)/4\pi r \qquad (1.57(c))$$

Both these operators approach the Fermi contact operator in the limit as $K \to \infty$.

Using the operator given in Eq. 1.57 in an exact first order perturbation calculation for the H atom yields the following expression for φ_1^{1s}:

$$\varphi_1^{1s}(r) = \varphi_{1,\ell}^{1s}(r) + \varphi_{1,s}^{1s}(r) \qquad (1.58)$$

where $\varphi_{1,\ell}^{1s}(r) = \left(\frac{K}{K+2}\right)^3 \left[\left(\frac{-2}{r}\right) + 4\ln r + 4r + C_{1s}\right] \varphi_0^{1s}(r)$ (1.58(a))

and $$\varphi^{1s}_{1,S}(r) = \left(\frac{K}{K+2}\right)^3 \left[\frac{(K+2)^2}{K} \exp(-Kr) + \frac{2}{r}\exp(-Kr) + 4E_1(Kr)\right]\varphi^{1s}_0(r) \quad (1.58(b))$$

This function has been separated into a "short-range" part, which rapidly decreases within the subatomic region $0 \leq r \leq 10/K$, and a "long-range" part which reaches to atomic molecular dimensions. Note that the long-range part which is contained in square brackets is identical to the solution for the Fermi contact operator given by Schwartz (Eq. 1.53). The "short-range" part allows φ^{1s}_1 to have a very large but finite negative value at the origin. This operator and wave function produce a finite second order energy but the first order energy now deviates in the 5th significant figure from the rather exact value obtained using the delta function. While this difference does not seem large, it does become significant when second order corrections are added to the total energy. The second order energy is about four orders of magnitude smaller than the first order term, so any second order corrections to the total energy become meaningless because the error in the first order energy is of the same order of magnitude as the second order term. In fact, the second order energies calculated using the operators in Eq. 1.54, 1.56, and 1.57 are two orders of magnitude too large.[48] (See

Table 2 for a comparison of the first and second order splitting energies calculated for the H atom using the operators discussed in this section.) This problem is discussed later in this chapter.

Dingle also calculated the "second order" hyperfine splitting energy of the H atom using the operator given in Eq. 1.57 in a variational calculation. His original wave function had the form:

$$\tilde{\varphi}_v(r) = \varphi_o^{1s}(r) + c_1 e^{-\alpha_1 r} + c_2 e^{-\alpha_2 r} + c_3 e^{-\alpha_3 r} \quad (1.59(a))$$

Using the $V_2(r)$ form of the operator, a variational treatment using this wave function gave slightly worse results for the second order energy than the perturbation method (see Table 2). A later, more accurate wave function was slightly more complex:

$$\tilde{\varphi}'_v(r) = \varphi_o^{1s}(r) + c_1 \left[\frac{e^{-\alpha r} - e^{-\beta r}}{r}\right] + c_2 r e^{-\delta r} \quad (1.59(b))$$

This wave function gave better results than the perturbation method when the exponents α, β, and δ were varied, but is still simpler than the first order perturbation wave function in Eq. 1.58. This suggests that reasonably accurate results for the molecular coupling constant could be obtained from variational calculations by using simpler trial wave functions than those derived directly from the first order perturbation function for the H atom.

Sänger and Voitlander performed an approximate (one-electron) calculation of J_{3HD} using an operator similar to

Table 2

1st and 2nd Order Hyperfine Splitting Energies of the

H atom as Calculated using the Operators Discussed in Section 1.4

Wave Function		1st Order Energy ($E_{1s}^{(1)}$)		2nd Order Energy ($E_{1s}^{(2)}$)	
Name	Equation	Equation	Numerical Value (Hartrees)[a] x 10^{-7}	Equation	Numerical Value (Hartrees)[a] x 10^{-9}
Delta Function (see Schwartz[19])	1.52, 1.53	$E_{1s}^{(1)} = \lambda^{b}$	2.16002	$E_{1s}^{(2)} = -\lambda^{2} \sum_{n}{}' \frac{\langle o \vert \frac{\delta(r)}{r^2} \vert n \rangle^2}{E_o - E_n}$	$-\infty$
Blinder Operator (see Blinder[41] and Power and Pitzer[44])	1.54, 1.55	$E_{1s}^{(1)} = \left[1 - \frac{2}{K} e^{2r_o} E_1\left(\frac{2}{K}\right)\right] \lambda^{c}$	2.15941	$E_{1s}^{(2)} = -\lambda^{2} \left(2K - \frac{1}{4} \ln \frac{\gamma}{K} + \frac{1}{4}\pi^2 - \frac{17}{4}\right)^{c}$	-3.5068
Gregson, Hall, and Rees Operator[42]	1.56	$E_{1s}^{(1)} = [K/(K+2)]\,\lambda$	2.15991	$E_{1s}^{(2)} = -\lambda^{2} \left(-\frac{5}{2} + (K-4)\ln 2 + \ln K\right)$	-1.2149
Dingle-Voitlander Operator[49,51,52,53]	1.57, 1.57(b), 1.58	$E_{1s}^{(1)} = [K/(K+2)]^3 \lambda = (1 - 6/K + \ldots)\lambda$	2.15967	$E_{1s}^{(2)} = -\lambda^{2} \frac{K^6}{(K+2)^6} \left[\frac{5K}{32} + \frac{51}{32} + \ldots\right]^{d} = +\lambda^{2} \left[-5K/32 + \ln(1/K) + 2\ln 2 + 7/32\right]$	-.27423
Alternate Dingle Operator	1.57, 1.57(c), 1.58	$E_{1s}^{(1)} = [K/(K+2)]^2 \lambda$	2.15979	$E_{1s}^{(2)} = -\lambda^{2} \frac{K^4}{(K+2)^4} \left[\frac{K}{4} + \frac{9}{4} + \ldots\right]^{e}$	-.43854
Alternate Dingle Operator (Variational Calculation)	1.57, 1.57(c), 1.59(a)		2.15984		-.435139
	1.57, 1.57(c), 1.59(b)		2.15984		-.439424
Experimental[69]			2.1604371		

a These energies can be converted to frequency units (Hz) by dividing by 1.521×10^{-16}

b $\lambda = Q_n/\pi = 2.16002 \times 10^{-7}$

c $K = 1/r_o = 2c^2 = 37559.38$ a.u.

d The full expansion of this energy is $E_{1s}^{(2)} = \lambda^{2} \frac{K^6}{(K+2)^6} \left[-\frac{5K}{32} - \frac{51}{32} + \ln\frac{2(K+1)}{(K+2)^2} + \frac{3}{4K} - \frac{9}{16(K+1)} + \frac{3}{K+2} - \frac{1}{16(K+1)^2} + \frac{5}{32K(K+1)} + \frac{1}{32K(K+1)^2}\right]$

e The full expansion of this energy is $E_{1s}^{(2)} = -\lambda^{2} \frac{K^4}{(K+2)^4} \left[\frac{K}{4} + \frac{9}{4} + \ln\frac{(K+2)^2}{4(K+1)} - \frac{2}{K+2} + \frac{1}{4(K+1)}\right]$

that in Eq. 1.57[52,53]:

$$\omega_N(i) = Q_N \left(\frac{K^3}{8\pi}\right) \exp(-K r_{iN})\, S_{zi}\, I_z^N \qquad (1.60)$$

where N = H,D (nuclei), i = 1,2 (electrons)

Since their trial wave function was based on the exact solution of the first order perturbation equation of atomic hydrogen in the 1s state (Eq. 1.58), it contained some fairly complex terms:

$$\tilde{\Psi}_1^H = \left[\tilde{\Phi}_1^H \Phi_0 - \Phi_0 \tilde{\Phi}_1^H\right] \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \qquad (1.61)$$

where $\Phi_0 = N_0 (\varphi_0^H + \varphi_0^D)$ (1.61(a))

$$N_0 = \left[2(1 + \langle \varphi_0^H | \varphi_0^D \rangle)\right]^{-1/2}$$
$$= \left[2(1+S)\right]^{-1/2} \qquad (1.61(b))$$

$$\varphi_0^N = \left(\frac{\epsilon^3}{\pi}\right)^{1/2} \exp(-\epsilon r_N), \quad N = H,D \qquad (1.61(c))$$

i.e., Φ_0 is the simplest LCAO-MO type wave function representing the ground state of HD such that:

$$\Psi_0 = \left[\Phi_0\, \Phi_0\right] \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \qquad (1.61(d))$$

$$\tilde{\Phi}_1^H = \tilde{C}_H \left(\tilde{\varphi}_1^H + C_1 \varphi_0^H + C_2 \varphi_0^D\right) I_z^H \qquad (1.61(e))$$

where $\tilde{\varphi}_1^H = \tilde{\varphi}_{1,s}^H + \tilde{\varphi}_{1,l}^H$ (1.61(f))

"s" denotes the short range ($< \frac{10}{K}$ away from the nucleus) part of the wave function

"l" denotes the long-range part of the wave function

$$\tilde{\varphi}^{H}_{1,s} = -K \exp(-k_1 K r_H) \times [k_1 K r_H + 1] \varphi^{H}_{o} \qquad (1.61(g))$$

$$\tilde{\varphi}^{H}_{1,\ell} = +k_2 r_H \varphi^{H}_{o} \qquad (1.61(h))$$

where k_1, k_2 are constants obtained by fitting φ^{H}_{o} to the first order perturbation function for the H atom.

The results obtained were good when the cross-coupling energy was made stationary (39.01 Hz) but were somewhat poorer if the total energy or the self-coupling energy alone was minimized.

Pyykkö[48] criticized both the Blinder/GHR and Voitlander-Dingle type operators because the hyperfine self-coupling energy derived from a first order perturbation calculation is over two orders of magnitude too large (see Table 2). This could lead to inaccuracies in the molecular coupling constant calculations, since a coupling constant which is dependent upon the self-coupling term may also be unphysical. Pyykkö analyzed both Paviot and Hoarau's GHR calculations[45,46] and Sänger and Voitlander's calculations using the operator in Eq. 1.60 to determine the dependence of the cross-coupling energy E_{3HD} on the self-coupling energy E_{3HH}. While Paviot and Hoarau's

trial function was similar in form to Sänger and Voitlander's (Eq. 1.61), the variational parameters were different: $\mathcal{K}$ in Eq. 1.61(g) and 1.61(f) was held constant and k_1 and k_2 were varied independently. Thus it appears that Paviot and Hoarau's cross-coupling energy was not dependent on the self-coupling term, but that Sänger and Voitlander's was dependent and is perhaps unphysical. Sänger and Voitlander referred to Moore and Moss' discussion of the Fermi contact interaction in the hydrogen atom[50] and suggested that the large "self-coupling" (hyperfine splitting) energies could be due to neglect of the first order terms quadratic in the vector potential (Eq. 1.19(e)).

In a later calculation[54], Sänger and Voitlander modified their trial wave function in order to eliminate the dependence of E_{3HD} on E_{3HH}. The new trial function contained both a long range and short range variational parameter:

$$\tilde{\Phi}_1^H = \left[\tilde{c}_s^H \tilde{\Phi}_s^H + \tilde{c}_\ell^H \tilde{\Phi}_\ell^H \right] I_2^H \tag{1.62}$$

where $\tilde{\Phi}_s^H = c_1^s \varphi_0^H + c_2^s \varphi_0^D + \tilde{\varphi}_{1,s}^H$ (1.62(a))

and $\tilde{\Phi}_\ell^H = c_1^\ell \varphi_0^H + c_2^\ell \varphi_0^D + \tilde{\varphi}_{1,\ell}^H$ (1.62(b))

φ_0^N, $\tilde{\varphi}_{1,s}^H$, $\tilde{\varphi}_{1,\ell}^H$ as in Eq. 1.61

$\tilde{\varphi}^{H}_{1,s}$ can be interpreted as the wave function of the electron "entering" the perturbing nucleus (contact) and leading to the self-coupling term, while $\tilde{\varphi}^{H}_{1,e}$ describes the electron carrying its spin polarization away from the perturbing nuclear spin. Since the second order energies calculated from the short and long range parts differ greatly in order of magnitude they can be varied independently. Sänger and Voitlander solved the resulting system of linear inhomogeneous equations and determined that the coupling constant appeared to be independent of the short range variational parameters $\tilde{c}^{N}_{s}$ and hence of the short range term to the order $O(1/K)$. Using this procedure, the results obtained by minimizing the entire second order energy are now equivalent to those obtained by making the cross-term energy stationary (39 Hz) or by varying one of the self-coupling terms and employing only the long range parts of the wave function.

Hoarau and another colleague, M.T. Rayez-Meaume, later developed an alternative method of dealing with the singularities caused by the Fermi contact operator[47]. In this approach, the delta function was removed by a transformation which allowed a minimization of a finite part of the second order energy. (The remainder of the self-coupling energy was still infinite but did not need to be determined since it did not depend on the functions

containing the variational parameters.) While the results using this approach were low, especially in the absence of configuration interaction, the convergence with increasing size of the basis set was greatly improved over the GHR results.[45,46] Hoarau had worried about the accuracy of the previous calculations because of large differences between some of the integrals used in the energy equations. These large differences did not appear in the set of calculations using the transformation operator. Since Rayez-Meaume and Hoarau did not distinguish between the GHR and Voitlander-Dingle operators in discussing this possible inaccuracy, spin-spin coupling calculations using the latter operator (as described in Chapter 2) should be checked for similar instability.

The transformed Fermi-contact operator of Rayez-Meaume and Hoarau is interesting, but it has not been fully tested. Furthermore, its use is hampered by the fact that the operator transformation complicates the calculations. Hoarau's research group tend to use complex trial wave functions to begin with; in the GHR calculations the trial wave functions had the form:

$$\Psi_{10} = (\text{constant}) \sum_i F_{iH} S_{iz} \Psi_{00} \qquad (1.63)$$

$$\text{where } F_{iH} = \sum_{K=1}^{n} a_K^H f_K^H (i) \qquad (1.63(a))$$

$$f_1^H(i) = \frac{1}{r_{iH}} \qquad (1.63(b))$$

$$f_2^H(i) = \log r_{iH} \qquad (1.63(c))$$

$$f_K^H(i) = r_{iH}^{(k-2)} \quad \text{for } k > 2 \qquad (1.63(d))$$

The wave function used by Rayez-Meaume and Hoarau in the transformation calculations was:

$$\psi_N = F_N \psi_0 + \varphi_N \qquad (1.64)$$

where $$F_N = C_N \sum_i \left(\frac{-2}{r_{iN}}\right) S_{iz} \qquad (1.64(a))$$

and $$\varphi_N = \sum_k a_k^N \phi_k \qquad (1.64(b))$$

where the ϕ_k represent excited state atomic orbitals (usually Slater-type orbitals) and the a_k are variational parameters.

The $\frac{1}{r_{iN}}$, $\log r_{iN}$, and $r_{iN}^{(k-2)}$ terms in Eq. 1.63 and 1.64 were apparently chosen because similar terms appear in the solution of the first order perturbation equation for hyperfine splitting in the H atom. If the method is to be applied to a wide range of hydrogen-containing molecules, complexities in the operator and in the trial wave function are clearly a drawback.

The search for a relatively simple form of trial wave function which will yield a good and reliable result

for J_{3HD} with a minimum of computation constitutes a large portion of this thesis. Sänger and Voitlander demonstrated that even an approximate, one-electron determination of J_{3HD} using the Voitlander-Dingle operator (Eq. 1.60) can yield good results if only the long-range contribution to the trial wave function is used in the calculations. Dingle's variational calculation of hyperfine splitting in the H atom gave slightly worse results than the Sänger-Voitlander perturbation calculations and used a simple trial wave function:

$$\tilde{\varphi}_v(r) = \varphi_0^{1s}(r) + c_1 e^{-\alpha_1 r} + c_2 e^{-\alpha_2 r} + c_3 e^{-\alpha_3 r} \quad (1.59(a))$$

This suggests that fairly simple wave functions will also yield comparable results to the more complicated ones used by Sänger and Voitlander in their variational calculation of J_{3HD}. Two sets of calculations are presented in this thesis:

(1) One-electron perturbation-variation calculations similar to those of Sänger and Voitlander but using simpler trial functions. Two different wave functions are considered:

(i) a trial wave function containing both short and long range terms

(ii) a trial wave function containing long range terms only

(2) Two-electron variational calculations of J_{3HD}.

In this more rigorous approach, both the ground state and trial wave function are composed of simple LCAO-MO functions:

$$\Psi_1 = c_0 \Psi_0 + c_T \Psi_T \qquad (1.65)$$

where $\Psi_0 = \Phi_0 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$

x nuclear spin functions (1.65(a))

$$\Psi_T = \Phi_T$$

x triplet electronic spin function

x nuclear spin functions (1.65(b))

where (1.65(c))

$$\Phi_0 = \phi_0 \phi_0 \text{ or } \phi_0 \phi_0 - c_F \phi_0' \phi_0'$$

$$\Phi_T = \frac{1}{\sqrt{2}} (\phi_1 \phi_2 - \phi_2 \phi_1) \qquad (1.65(d))$$

where ϕ_0, ϕ_0' are ground state wave functions

(ϕ_0 symmetric, ϕ_0' antisymmetric)

and ϕ_1, ϕ_2 are trial wave functions

(ϕ_1 symmetric, ϕ_2 antisymmetric)

The results of these calculations are presented in Chapter 2. Although the results of the two-electron calculations to date have not been impressive, the operator should give better results for wave functions which more adequately describe the effects of spin-spin coupling on the electronic distribution in the molecule. Chapter 3

consists of a discussion on the form of trial wave function which should be most suitable for future two-electron calculations. While such a wave function could result in self-coupling energies which are too large and hence unphysical, this inaccuracy is due to spurious terms arising from the form of the operator and it is speculated that these terms will cancel in the cross-coupling energy calculation. The wave function should yield a good result for J_{3HD} without excessive computations and be relatively easy to transfer from molecule to molecule in order to facilitate a general method of calculating spin-spin coupling between hydrogen atoms.

CHAPTER 2

CALCULATIONS OF J_{3HD}

2.1 ONE-ELECTRON CALCULATIONS

Sänger and Voitlander performed a number of calculations of the contact contribution to the spin-spin coupling constant of HD.[52,53,54] Since the purpose of their calculations was to study the qualitative consequences of introducing a phenomenological non-singular contact perturbation into the problem, they chose an approximate, one-electron method in order to avoid mathematical and computational difficulties which would occur in two-electron calculations.

The one-electron perturbation Hamiltonian is:

$$\mathcal{H} = \sum_{i=1}^{2} [h_0(i) + Q_H \omega_H(i) + Q_D \omega_D(i)] + 1/R$$

$$= \sum_{i=1}^{2} [h_0(i)] + Q_H \sum_{i=1}^{2} \omega_H(i) + Q_D \sum_{i=1}^{2} \omega_D(i) + 1/R$$

$$= \mathcal{H}_0 + Q_H \mathcal{H}^H_{3ns} + Q_D \mathcal{H}^D_{3ns} \qquad (2.1(a))$$

where $h_0(i) = -\frac{\nabla_i^2}{2} - \frac{(1-\sigma)}{r_{iH}} - \frac{(1-\sigma)}{r_{iD}}$ (2.1(b))

R is the internuclear distance and in the calculations presented here is set equal to the equilibrium distance for H_2 (R_e= 1.4)

σ (=0.2) is an electronic screening constant which represents approximately an average of the two-electron repulsion terms

the Q_N are constants representing the strength of the electron-nucleus spin-spin coupling interaction:

$$Q_N = \frac{8\pi}{3} g_e \beta_e g_N \beta_N \qquad (2.1(c))$$

For simplicity's sake, the contact perturbation can be taken to be isotropic so that nuclear spins are chosen to be definitely quantized in the z-direction. The perturbation operators $\omega_N(i)$ which represent the contact interactions between the 1s electrons and the nucleus N are given by:

$$\omega_N(i) = \frac{K^3}{8\pi} \exp(-K r_{iN}) S_{zi} I_z^N \qquad (2.1(d))$$

where K is a phenomenological parameter which describes a spatial extension of the magnetic moment distribution. Typically $K^{-1} = 10^{-5}$ a.u.

It is not necessary to integrate over the operator in Eq. 2.1(a) directly. Using the Dalgarno interchange theorem[27,58,59] (see Appendix 1), it is possible to express the perturbation energies of a singly perturbed Hamiltonian

$$\begin{aligned} \mathcal{H}_P &= \mathcal{H}_{00} + \mu \mathcal{H}_{10} \\ &= \mathcal{H}_0 + Q_H \omega_H(1,2) \end{aligned} \tag{2.2}$$

where $$\omega_H(1,2) = \omega_H(1) + \omega_H(2) \tag{2.2(a)}$$

The expression for $\tilde{E}_{3HD}$ is obtained by substituting $\omega_H(1,2)$ for $\mathcal{H}_{10}$, $\tilde{\Psi}_1^H$ for Ψ_{10}, and $\tilde{\Psi}_1^D$ for Ψ_{01} into Eq. A1.26(a):

$$\begin{aligned} Q_H Q_D \tilde{E}_{3HD} &= 4 \langle \Psi_0 | Q_H \omega_H(1,2) | Q_D \tilde{\Psi}_1^D \rangle \\ &\quad + 2 \langle Q_H \tilde{\Psi}_1^H | \mathcal{H}_0 - E_0 | Q_D \tilde{\Psi}_1^D \rangle \end{aligned} \tag{2.3}$$

Similarly, the expression for E_{3HH} (= E_{3DD} by symmetry) is derived from Eq. A1.24:

$$\begin{aligned} Q_H^2 \tilde{E}_{3HH} &= 2 \langle \Psi_0 | Q_H \omega_H(1,2) | Q_H \tilde{\Psi}_1^H \rangle \\ &\quad + \langle Q_H \tilde{\Psi}_1^H | \mathcal{H}_0 - E_0 | Q_H \tilde{\Psi}_1^H \rangle \end{aligned} \tag{2.4}$$

Equations 2.3 and 2.4 can be reduced by summing over spins in the one-electron scheme:

$$Q_H Q_D \tilde{E}_{3HD} = \lambda \{ 2 \langle \Phi_0 | Q_H \omega_H(1) | Q_D \tilde{\Phi}_1^D \rangle + \langle Q_H \tilde{\Phi}_1^H | h_0 - \varepsilon_0 | Q_D \tilde{\Phi}_1^D \rangle \} \tag{2.5}$$

$$Q_H^2 \tilde{E}_{3HH} = \lambda \langle Q_H \tilde{\Phi}_1^H | Q_H \omega_H(1) | \Phi_0 \rangle + 2 \langle Q_H \tilde{\Phi}_1^H | h_0 - \varepsilon_0 | Q_H \tilde{\Phi}_1^H \rangle \tag{2.6}$$

where Φ_0 and $\tilde{\Phi}_1^N$ are the spatial parts of the zeroth order (ground state) and first order (trial variational) wave functions respectively. ε_0 is essentially a simple LCAO/MO approximation to the molecular energy of H_2^+:

$$\varepsilon_0 = \langle \Phi_0 | h_0 | \Phi_0 \rangle \tag{2.7}$$

For Φ_0, Sänger and Voitlander chose a simple LCAO-MO type function:

$$\Phi_0 = N_0 (\varphi_0^H + \varphi_0^D) \tag{2.8(a)}$$

where $$\varphi_0^N = \left(\frac{\epsilon^3}{\pi}\right)^{1/2} \exp(-\epsilon r_N) \tag{2.8(b)}$$

and $$N_0 = [2(1 + \langle \varphi_0^H | \varphi_0^D \rangle)]^{-1/2} \tag{2.8(c)}$$

The exponential scaling parameter was set equal to 1.2 (If the function in Eq. 2.8 is used in a variational

calculation of the electronic energy of H_2, where ϵ is the variational parameter, the minimum energy occurs at a value of $\epsilon = 1.1895$.)

Their first order (variational) wave functions had the form:

$$\tilde{\Phi}_1^N = \tilde{C}_N \left(\tilde{\varphi}_1^N + C_1 \varphi_o^H + C_2 \varphi_o^D \right) I_2^N \qquad (2.9(a))$$

where $\tilde{C}_N$ is a variational parameter and C_1, C_2 are determined by orthonormalization conditions:

$$\langle \tilde{\Phi}_1^N \mid \tilde{\Phi}_1^N \rangle = 1 \qquad (2.9(b))$$

$$\langle \Phi_o \mid \tilde{\Phi}_1^N \rangle = 0 \qquad (2.9(c))$$

$\tilde{\varphi}_1^N$ consisted of a short-range and a long-range part:

$$\tilde{\varphi}_1^N = \tilde{\varphi}_{1,s}^N + \tilde{\varphi}_{1,\ell}^N \qquad (2.9(d))$$

where $$\tilde{\varphi}_{1,s}^N = -K \exp(-k_1 K r_N) \times [k_1 K r_N + 1] \varphi_o'^N \qquad (2.9(e))$$

$$\tilde{\varphi}_{1,\ell}^N = k_2 r_N \varphi_o'^N \qquad (2.9(f))$$

$$\varphi_o'^{N} = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp(-\alpha r_N) \qquad (2.9(g))$$

α was set equal to 1.0

k_1, k_2 are fitting constants and the scaling parameter $\alpha = 1.0$, so that the trial function $\tilde{\varphi}_1^{H}$ gives a good fit to the atomic function (see Eq. 1.57) over the ranges $0 \leq r \leq 10/K$ and 0.1 a.u. $\leq r < \infty$

Essentially the long range part describes an electron carrying its spin polarization away from the perturbing nuclear spin and transferring this polarization via the chemical bond to the other nucleus, while the short range part describes the electron "in contact" with the perturbing nucleus.

The trial wave function seems complex and it would be difficult to extend this formulism to molecules which are not as simple as hydrogen deuteride. It was decided to perform an analogous calculation using the same operator but with a simpler trial function:

$$\tilde{\Phi}_1'^{N} = (\tilde{C}_N' \tilde{\varphi}_1'^{N} + C_1 \varphi_o^{H} + C_2 \varphi_o^{D}) I_z^{H} \qquad (2.10)$$

where $$\tilde{\varphi}_1'^{N} = \left(\frac{K^3}{\pi}\right)^{1/2} \exp(-K r_N) \qquad (2.10(a))$$

In this work, K was set equal to 30,000, i.e., the approximate value of K which gave the best energy when the

Voitlander-Dingle type operator was used in variational calculations of hyperfine splitting energy in the H atom (see Chapter 1). The scaling parameter ϵ in φ_0^N was set equal to the zero-order value ($\epsilon = 1.2$). Comparing Eq. 2.10(a) to Eq. 2.9(d) $\rightarrow$ (g) indicates that $\tilde{\varphi}_1^{/N}$ is essentially a short range function.

The value of $\tilde{C}_N$ may be determined by minimizing the total second order energy or the self-coupling energy only, or by making the cross-coupling energy stationary. It was decided to minimize the self-coupling energy (given by Eq. 2.6) since this method is given in most detail by Sänger and Voitlander[53] and the comparison is hence more direct than for the other methods.

If the wave function $\tilde{\Phi}_1^N$ or $\tilde{\Phi}_1^{/N}$, determined by minimizing $\tilde{E}_{HH}$ with respect to $\tilde{C}_H$, is exact, then:

$$\langle \Phi_0 | \omega_H(1) | Q_D \tilde{\Phi}_1^D \rangle = -\langle Q_H \tilde{\Phi}_1^H | h_0 - \varepsilon_0 | Q_D \tilde{\Phi}_1^D \rangle \qquad (2.11)$$

(see Appendix 1, Eq. A1.20). The cross-coupling energy then reduces to:

$$Q_H Q_D \tilde{E}_{3HD} = \tfrac{1}{2} \langle \Phi_0 | Q_H \omega_H(1) | Q_D \tilde{\Phi}_1^D \rangle \qquad (2.12)$$

Conversion to the coupling constant is straightforward:

$$J_{3HD} = (2\pi)^{-1} Q_H Q_D \tilde{E}_{3HD} (I_2^H I_2^D)^{-1} \quad (2.13)$$

In order to convert from atomic units to cycles per second, Eq. 2.13 must be divided by a factor of 1.521×10^{-16}.

The calculation of J_{3HD} using $\tilde{\Phi}_1^{/N}$ consisted of two steps:

1) Determination of $\tilde{C}_H$ by minimizing $\tilde{E}_{3HH}$

2) Calculation of J_{3HD} using Eq. 2.12 and 2.13.

Both these steps were carried out using the University of Victoria's IBM 370 computer. The programming required three main types of subroutines:

1) A minimization subroutine. This routine was based on the Fibonacci search method, which is highly efficient for one parameter minimizations.

2) A subroutine to solve for the orthonormalization constants C_1 and C_2 (see Eq. 2.9). Since the values of C_1 and C_2 depend upon the value of the variational parameter $\tilde{C}_H$, C_1 and C_2 had to be recalculated for each iteration of the minimization subroutine. Solution of C_1 and C_2 consisted of solving a quadratic equation determined by solving Eq. 2.9(b) and 2.9(c) simultaneously. The subroutine was based on the Pegasus method.

3) Various functional subroutines to calculate the integrals required by Eq. 2.6 and 2.12.

(a) $\langle Q_H \tilde{\Phi}_1'^H | h_o - \varepsilon_o | Q_H \tilde{\Phi}_1'^H \rangle$

$$= \{ \langle \varphi_1'^H | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle + 2\langle \varphi_o^H | h_o - \varepsilon_o | \varphi_o^H \rangle + 2\langle \varphi_o^H | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle + 2\langle \varphi_o^D | h_o - \varepsilon_o | \varphi_o^H \rangle + 2 \langle \varphi_o^D | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle \} Q_H^2$$

(2.14)

The integrals containing only φ_o^N functions were calculated using the formulae given by Slater[62] for calculation of the molecular electronic energy of H_2 (Chapters 3 and 4). The $\langle \tilde{\varphi}_1'^H | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle$ and $\langle \varphi_o^H | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle$ integrals were also based on these formulae but the subroutines had to be modified to cope with the large magnitude of the perturbation parameter, K, and the presence of two different exponential parameters (ϵ, K). The $\langle \varphi_o^D | h_o - \varepsilon_o | \tilde{\varphi}_1'^H \rangle$ integral was based on formulae given by McGlynn et al[65] for general overlap integrals (Chapter 2). Once again the subroutines had to be modified to cope with the magnitude of K.

(b) $\langle Q_H \tilde{\Phi}_1'^H | Q_H \omega_H(1) | \Phi_0 \rangle$ and

$\langle \Phi_0 | Q_H \omega_H(1) | Q_D \tilde{\Phi}_1'^D \rangle$

These integrals expand into a summation of overlap-type integrals. For example:

$$\langle Q_H \tilde{\Phi}_1'^H | Q_H \omega_H(1) | \Phi_0 \rangle$$

$$= \{ C_1 (\langle \varphi_0^H | Q_H \omega_H(1) | \varphi_0^H \rangle + \langle \varphi_0^H | Q_H \omega_H(1) | \varphi_0^D \rangle) + C_2 (\langle \varphi_0^D | Q_H \omega_H(1) | \varphi_0^H \rangle + \langle \varphi_0^D | Q_H \omega_H(1) | \varphi_0^D \rangle) + \tilde{C}_H (\langle \tilde{\varphi}_1'^H | Q_H \omega_H(1) | \varphi_0^H \rangle + \langle \tilde{\varphi}_1'^H | Q_H \omega_H(1) | \varphi_0^D \rangle) \} N_0 Q_H$$

$$= N_0 Q_H^2 \{ C_1 (\exp[-(2\epsilon+K)r_H] + \langle \exp[-(\epsilon+K)r_H - \epsilon r_D] \rangle + C_2 (\langle \exp[-(\epsilon+K)r_H - \epsilon r_D] \rangle + \langle \exp[-2\epsilon r_D - K r_H] \rangle) + \tilde{C}_H (\langle \exp[-2K+\epsilon)r_H] \rangle + \langle \exp[-2K r_H - \epsilon r_D] \rangle) \} \quad (2.15)$$

The expansion of $\langle \Phi_0 | Q_H \omega_H(1) | Q_D \tilde{\Phi}_1'^D \rangle$ is similar. Those integrals involving only one nucleus were calculated using formulae based upon those of Slater and those involving both nuclei were calculated using formulae based upon those of McGlynn et al, with suitable modifications to cope with the magnitude of K.

The expression for the self-coupling energy (Eq. 2.6) requires a value for the ground state energy,

$\mathcal{E}_o$, which can be calculated by solving the integral in Eq. 2.7. Since this is essentially a simple LCAO/MO approximation to the molecular electronic energy of H_2^+, this integral contains terms similar to those needed to perform a simple LCAO/MO calculation for H_2. All necessary formulae are given by Slater. The programme used to calculate $\mathcal{E}_o$ expressed the energy as a function of the exponential parameter ϵ, the internuclear distance R, and the screening constant σ, which allowed for a check against the values given by Slater in Chapter 2. For $\epsilon = 1.2$, $R = 1.4$, and $\sigma = 0.2$, $\mathcal{E}_o = -.886$ a.u.

The results of the computations of $\tilde{E}_{3HH}$ and J_{3HD} are given in Table 3. The equation given for $\tilde{E}_{3HD}$ in this thesis (Eq. 2.12) differs from Sänger and Voitlander's equation for $\tilde{E}_{3HD}$ (Eq. 33 in Ref. 53) by a factor of four. Checking the derivation of this equation indicates that the factor of four should, in fact, be included. This factor does appear in Sänger and Voitlander's equations for $\tilde{E}_{3HD}$ which are derived for the cases where the total second order energy is minimized and the cross-coupling energy made stationary (Eq. 37 and 38 in Ref. 53), so it appears that it was omitted from Eq. 33. If their result for J_{3HD} which is obtained by first minimizing the self-coupling energy is multiplied by four, it agrees with the value obtained from the calculations

presented here.

As noted by Pyykkö[48] (see Section 1.4), the self-coupling energy calculated by this method is much too large. If the trial function has only one variational parameter, as it does for both $\tilde{\Phi}_1^N$ and $\tilde{\Phi}_1'^N$, the cross-coupling energy depends upon the self-coupling energy and may also be unphysical. Sänger and Voitlander reformulated the problem so that the short and long range parts of $\tilde{\Phi}_1^N$ could be varied independently:

$$\tilde{\Phi}_1^N = \left[\tilde{C}_s^N \tilde{\Phi}_s^N + \tilde{C}_\ell^N \tilde{\Phi}_\ell^N \right] I_2^N \tag{2.16}$$

where

$$\tilde{\Phi}_s^N = C_1^s \varphi_0^H + C_2^s \varphi_0^D + \tilde{\varphi}_{1,s}^N \tag{2.16(a)}$$

$$\tilde{\Phi}_\ell^N = C_1^\ell \varphi_0^H + C_2^\ell \varphi_0^D + \tilde{\varphi}_{1,\ell}^N \tag{2.16(b)}$$

and φ_0^H, φ_0^D, $\tilde{\varphi}_{1,s}^N$, $\tilde{\varphi}_{1,\ell}^N$ are as given in Eq. 2.9

Since the second order energies calculated from the short and long range parts differ greatly in order of magnitude, Sänger and Voitlander varied the two parts independently:

$$\frac{\partial \tilde{E}^{(2)}}{\partial \tilde{C}_s^N} = \frac{\partial \tilde{E}^{(2)}}{\partial \tilde{C}_\ell^N} = 0 \tag{2.17}$$

Solving the linear inhomogeneous system so obtained, they concluded that the heterocoupling energy $\tilde{E}_{3HD}$ was independent of the short range parameters $\tilde{C}_s^N$ to the order $O(1/K)$. The numerical result obtained by minimizing the entire second order energy was 39 Hz, which is very close to the experimental value. Varying one of the self-coupling terms using the long range parts defined in 2.16(b) or making the cross-coupling energy stationary yielded the same result.

If the short range term in Eq. 2.10 is omitted, the result is a non-variational function:

$$\tilde{\Phi}_1^{\prime N} = (C_1 \varphi_o^H + C_2 \varphi_o^D) I_z^H \qquad (2.18)$$

where $C_1 = -C_2$ since the first order function must be orthogonal to $\bar{\Phi}_o$ and hence antisymmetric. Since this function is not an exact first order solution, the cross-coupling energy cannot be calculated using Eq. 2.12 so Eq. 2.5 must be used. Substituting Eq. 2.5 into Eq. 2.13 allows a direct calculation of J_{3HD} without variation. The programme used for the variational calculations including the short range part of the wave function was modified to bypass the minimization process and set $\tilde{C}_H$ to zero. As predicted, the solution of the orthonormalization parameters gave $C_1 = -C_2$. The results for $\tilde{E}_{3HH}$ and J_{3HD} are given in Table 3. Once again the

Table 3

Results of the One-electron Calculations of J_{3HD}

Parameter	Trial function including short range term		Trial function with long range terms only	
$\tilde{C}_H$	1.2×10^{-3}		—	
Coupling energy	Hartrees	Hz	Hartrees	Hz
$Q_H^2\tilde{E}_{3HH}$	-1.55×10^{-11}	-1.02×10^{5}	-3.06×10^{-14}	-201
J_{3HD}	1.03×10^{-14}	67.7	5.98×10^{-15}	39.3

Table 4

Dependence of the Coupling Constant J_{3HD} and the Self-Coupling Energy $\tilde{E}_{3HH}$ on the Scaling Parameter ϵ

	J_{3HD}*(Hz)	$Q_H^2\tilde{E}_{3HH}$*(Hartrees)
0.5	-48.2	3.74×10^{-14}
1.0	6.71	-5.23×10^{-15}
1.2	39.3	-3.06×10^{-14}
1.5	116	-9.05×10^{-14}
2.0	328	-2.55×10^{-13}

* J_{3HD} and $\tilde{E}_{3HH}$ were calculated using the long-range-only trial wave function given in Eq. 2.18

hetero coupling constant was identical (to two significant figures) to the value obtained by Sänger and Voitlander. While the self-coupling energy calculated using the trial function in Eq. 2.18 cannot be taken as exact since the zero order function is not exact, the magnitude is vastly improved over the result obtained when the short range term is included.

One of the more notable aspects of the one-electron results presented here is their agreement with those of Sänger and Voitlander, even though in both the short-range-included and short-range-deleted calculations the trial wave functions $\tilde{\Phi}_1^{'N}$ and $\tilde{\Phi}_1^{N}$ are not the same. Sänger and Voitlander's trial wave functions were more complex (i.e. contained more terms) than those presented here. Comparing Eq. 2.9 with Eq. 2.10 shows that, in both sets of calculations, the $k_2 r_N \varphi_0^{'N}$ term which is included in Eq. 2.9 was omitted from the long-range part of the wave function in Eq. 2.10, and that, in the short-range-included calculation, the short-range part of the wave function:

$$\tilde{\varphi}_{1,S}^{N} = -K \exp(-k_1 K r_N) \times [k_1 K r_N + 1] \varphi_0^{'N} \qquad (2.9(e))$$

$$= K^2 k_1 r_N \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp[-(k_1 K + \alpha) r_N] - K \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp[-(k_1 K + \alpha) r_N]$$

was replaced by:

$$\tilde{\varphi}_{1,s}^{\prime N} = \left(\frac{K^3}{\pi}\right)^{1/2} \exp(-Kr_N) \qquad (2.10(a))$$

The single term in Eq. 2.10(a) is somewhat similar to the second term in Eq. 2.9(e). (The first term is a multiple of r_N). It is possible that the omitted terms do not contribute much to the cross-coupling energies. However, the wave functions also differ in the scaling parameters used in the exponential terms. Sänger and Voitlander's scaling parameters ϵ (used in the ground state function Φ_o) and α (used in the trial function $\tilde{\Phi}_1^N$) are not linked (i.e. $\epsilon = 1.2 \neq \alpha = 1.0$) whereas they are linked ($\epsilon = \alpha = 1.2$) in the calculations presented here. The coupling constant <u>is</u> sensitive to the value of the scaling parameter; varying ϵ produces a range of values for J_{3HD} (see Table 4). This is not unexpected, since nuclear spin-spin coupling should be sensitive to the calculated electron density at the nucleus, which depends upon the value of the scaling parameter. Kolos and Wolniewicz[60] give the optimum density for the hydrogen molecule (which should be the same as that for HD) at the nucleus as .2299 a.u. Using the one electron approximation and taking as given in Eq. 2.8, the density ρ at the nucleus is related to the parameter ϵ as follows:

$$\rho(\epsilon R) = \frac{1}{2\pi(1+S(\epsilon R))}\left(1 + 2e^{-\epsilon R} + e^{-2\epsilon R}\right) \tag{2.19}$$

$$S(\epsilon R) = \langle \varphi_o^{H} | \varphi_o^{D} \rangle$$

$$= e^{-\epsilon R}\left(1 + \epsilon R + \frac{(\epsilon R)^2}{3}\right) \tag{2.19(a)}$$

The comparison of the known density H_2 at the nucleus with values of the density calculated using Eq. 2.19 was done using the computer. The programme selected the value of ϵ in Eq. 2.19 which yielded the best density match with the known value to ± .00005. If R = 1.4, ρ = .2299 when ϵ = 1.1977. This is very close to the value of 1.2 used in the calculations presented in this chapter.

The scaling parameter α has the same order of magnitude as the ground state scaling parameter ϵ, but it was assumed to have a negligible contribution to the density at the nucleus because it appears in the trial wave function only (the spin-spin coupling contribution to the total wave function is effectively just a small perturbation). Possibly this explains why changing its value has no discernible effect on the value of the coupling constant.

The coupling constant is not very sensitive to the value of the phenomenological parameter κ. The term $\exp(-\kappa r_N)$ represents a "peaking" of electron density at the nucleus due to the spin-spin coupling perturbation and, as long as κ is sufficiently large ($\gtrsim 3000$), it mimics the behavior of the Fermi contact operator without leading to infinities. If κ is multiplied by a factor of 10, the cross-coupling constant J_{3HD} changes by a mere 0.1 Hz.

There is an alternate hypothesis which may explain why the differences between Sänger and Voitlander's trial wave functions and the trial wave functions used in the preceding calculations seem to have no effect on the value of the coupling constant. It is possible that, under the constraints of the system, the minimization process (in the short-range-included case) and the relationship between the various terms in the formulae for the self-coupling and cross-coupling energies may adjust to compensate for changes in the scaling parameter ϵ and/or differences in the complexities of the wave functions $\tilde{\Phi}_1^{1/N}$ and $\tilde{\Phi}_1^{N}$. In the calculations including short-range functions, the variation constant $\tilde{c}_H$ is first determined by minimization and its value then substituted into Eq. 2.12 to calculate the cross-coupling energy. It is possible that the minimization process adjusts the value

of $\tilde{C}_H$ to compensate for the changes involved in substituting $\tilde{\Phi}_1^{IN}$ for $\tilde{\Phi}_1^{N}$. In the long-range-only calculations, the cross-coupling energy is given by:

$$Q_H Q_D \tilde{E}_{3HD} = 4\langle 2\langle \Phi_0 | Q_H \omega_H(1) | Q_D \tilde{\Phi}_1^{D} \rangle + \langle Q_H \tilde{\Phi}_1^{H} | h_0 - \varepsilon_0 | Q_D \tilde{\Phi}_1^{D} \rangle \qquad (2.5)$$

The two integrals are not equal when the wave functions are not exact, but it is possible that they are related in such a way that their values adjust to compensate for the differences between $\tilde{\Phi}_1^{N}$ and $\tilde{\Phi}_1^{IN}$ and hence give the same heterocoupling energy for both. If this is true, then the form of the trial wave function for this particular system is not too important. What is important is that, in order to obtain a cross-coupling constant which is not dependent on a minimized self-coupling energy which is unphysical, only the long-range parts of the trial wave function must be used to calculate the cross-coupling energy.

It should be noted that Rayez-Meaume and Hoarau[47] criticized Sänger and Voitlander's calculations because large differences in the integral values led to difficulties with the accuracy of the calculations. The calculations presented here were examined for such instabilities but none were found. Either the more complex terms in the

Sänger - Voitlander trial wave function were the source of the large differences or the criticism was invalid.

The one-electron calculations of Sänger and Voitlander and those presented here were intended to give a qualitative indication of the applicability of the spin-coupling operator given in Eq. 2.1; since the method is only an approximate one, it was not necessarily expected to give good results and certainly not meant to be extended to molecules other than the relatively simple HD. In fact, the result obtained for the long-range-only calculations was very close to the experimental value of J_{3HD}. This does not necessarily mean that two-electron calculations using the analogous two-electron form of the operator in Eq. 2.1 and similar trial wave functions containing only long-range terms will also give accurate values for J_{3HD}. Such calculations presented in the next section.

2.2 TWO-ELECTRON CALCULATIONS

The calculations in this section use the Voit-lander - Dingle operator in a series of variational spin-spin coupling calculations which include two-electron repulsion terms. In the one-electron calculations, the contact perturbation was assumed to be isotropic and the spin parts of the operator reduced to their z components. The derivation presented for the two-electron calculations uses the operator in its anisotropic form:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ns} \tag{2.20}$$

$$\text{where } \mathcal{H}_0 = \sum_{i=1}^{2} \left(-\frac{\nabla_i}{2} - \sum_{N=1}^{2} \frac{1}{r_N} \right) + 1/r_{12} + 1/R \tag{2.20(a)}$$

$$\mathcal{H}_{ns} = \sum_{i=1}^{2} \sum_{N=1}^{2} Q_{Ni} \hat{I}_N \cdot \hat{S}_i \tag{2.20(b)}$$

$$Q_{Ni} = \frac{Q_N K^3 \exp(-K r_{Ni})}{8\pi} \tag{2.20(c)}$$

$$Q_N = \frac{8\pi}{3} g_e \beta_e g_N \beta_N \tag{2.20(d)}$$

Since the derivation is easier for H_2 than for HD, both nuclei are chosen to be hydrogen. The coupling constant

for J_{3HD} can be calculated from J_{3HH} by substituting in Eq. 1.9:

$$J_{HD} / J_{HH} = \gamma_D / \gamma_H = 0.154 \qquad (1.9)$$

The variational trial function is assumed to have the form:

$$\tilde{\Psi}_1 = c_0 \Psi_0 + c_v \tilde{\Psi}_v \qquad (2.21)$$

where $\Psi_0 = \Phi_0 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$

x nuclear spin functions (2.21(a))

is the singlet (ground state) wave function and $\tilde{\Psi}_v = \tilde{\Phi}_v$ x electron triplet spin function x nuclear spin functions is a triplet (variational) wave function (2.21(b))

As is usual in a variational treatment, the total energy is given by the integral:

$$E = \frac{\langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle}$$

$$= \frac{\langle c_0 \Psi_0 + c_v \tilde{\Psi}_v | \mathcal{H}_0 + \mathcal{H}_{fns} | c_0 \Psi_0 + c_v \tilde{\Psi}_v \rangle}{\langle c_0 \Psi_0 + c_v \tilde{\Psi}_v | c_0 \Psi_0 + c_v \tilde{\Psi}_v \rangle} \qquad (2.22)$$

This integral can be expressed as a secular determinant. Since the operator given in Eq. 2.20 is anisotropic, all possible combinations of electron spin and nuclear spin

functions must be considered (see Table 5). This yields a 16 x 16 matrix consisting of singlet, triplet, and cross-term elements:

$$\left|\begin{array}{c|c} \langle \Psi_0 \mathcal{H} \Psi_0 \rangle - E \text{ terms} & \langle \Psi_0 \mathcal{H} \tilde{\Psi}_v \rangle - E \text{ terms} \\ (4\times 4) & (4\times 12) \\ \hline \langle \tilde{\Psi}_v \mathcal{H} \Psi_0 \rangle - E \text{ terms} & \langle \tilde{\Psi}_v \mathcal{H} \Psi_v \rangle - E \text{ terms} \\ (12\times 4) & (12\times 12) \end{array}\right| \qquad (2.23)$$

Fortunately many of the elements are zero due to the orthogonality of singlet and triplet wave functions under the operator:

$$\langle k \mathcal{H}_{ns} \ell \rangle = \delta_{k\ell} \langle k \mathcal{H}_{ns} k \rangle \quad \text{for } E_k = E_\ell \qquad (2.24)$$

Moreover, since all these functions are orthogonal under $\mathcal{H}_0$, it is sufficient to consider $\mathcal{H}_{ns}$ only. The determinant can be solved using standard linear algebraic techniques to give expressions for the wave function and energy. For the nuclear singlet, the wave function is given by:

$$\tilde{\Psi} = C_0 \Phi_0 |S_0 S_0\rangle + C_v \tilde{\Phi}_v \left|\frac{1}{\sqrt{3}}(-T_0 T_0 + T_+ T_- + T_- T_+)\right\rangle \qquad (2.25)$$

where $\Phi_0 = \phi_0(1)\,\phi_0(2)$ (2.25(a))

$$\tilde{\Phi}_v = (\phi_0(1)\phi_v(2) - \phi_v(1)\phi_0(2))\frac{1}{\sqrt{2}} \quad (2.25(b))$$

$$\phi_0 = N_0\left(\frac{\epsilon^3}{\pi}\right)^{\frac{1}{2}}(e^{-\epsilon r_{H_1}} + e^{-\epsilon r_{H_2}}) \quad (2.25(c))$$

where $N_0 = [2(1 + \langle e^{-\epsilon r_{H_1}} | e^{-\epsilon r_{H_2}} \rangle \frac{\epsilon^3}{\pi})]^{-\frac{1}{2}}$ (2.25(d))

$$\phi_v = \frac{\phi_v' - \phi_0\,\sigma_{0v}'}{\sqrt{1 - (\sigma_{0v}')^2}} \quad (2.25(e))$$

$$\phi_v' = N_v\left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}}(e^{-\alpha r_{H_1}} \pm e^{-\alpha r_{H_2}}) \quad (2.25(f))$$

where $N_v = [2(1 \pm \langle e^{-\alpha r_{H_1}} | e^{-\alpha r_{H_2}} \rangle \frac{\alpha^3}{\pi})]^{-\frac{1}{2}}$ (2.25(g))

$$\sigma_{0v}' = \langle \phi_0 \phi_v' \rangle \quad (2.25(h))$$

$$T_0 = \frac{1}{\sqrt{2}}(ab + ba) \quad (2.25(i))$$

$$T_+ = aa \quad (2.25(j))$$

$$T_- = bb \quad (2.25(k))$$

$$S_0 = \frac{1}{\sqrt{2}}(ab - ba) \quad (2.25(l))$$

The corresponding total energy is given by:

$$E = E_0 - \frac{\frac{3}{8}\left(q_{0v}^{(1)}\right)^2}{E_v - 2d - E} + \frac{\frac{3}{4} q_{0v}^{(1)} q_{0v}^{(2)}}{E_v - 2d - E} - \frac{\frac{3}{8}\left(q_{0v}^{(2)}\right)^2}{E_v - 2d - E} \qquad (2.26)$$

where $q_{0v}^{(1)} = \langle \phi_0 \, Q_{11} \, \phi_v \rangle$ (2.26(a))

$q_{0v}^{(2)} = \langle \phi_0 \, Q_{21} \, \phi_v \rangle$ (2.26(b))

$d = \frac{1}{2}\left(q_{00}^{(1)} + q_{vv}^{(2)}\right)$ (2.26(c))

$q_{00}^{(1)} = \langle \phi_0 \, Q_{11} \, \phi_0 \rangle$ (2.26(d))

$q_{vv}^{(1)} = \langle \phi_v \, Q_{11} \, \phi_v \rangle$ (2.26(e))

$E_0 = \langle \Phi_0 | \mathcal{H}_0 | \Phi_0 \rangle$ (2.26(f))

$E_v = \langle \tilde{\Phi}_v | \mathcal{H}_0 | \tilde{\Phi}_v \rangle$ (2.26(g))

Table 5

Possible Combinations of Electron Spin and Nuclear Spin Functions for the Anisotropic Hydrogen Molecule

Wave Function	Electron Spin Function	Nuclear Spin Function
ψ_o	$S_o = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$	$S_o = \frac{1}{\sqrt{2}}(ab - ba)$
		$T_+ = aa$
		$T_o = \frac{1}{\sqrt{2}}(ab + ba)$
		$T_- = bb$
ψ_v	$T_o = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$	$S_o = \frac{1}{\sqrt{2}}(ab - ba)$
	$T_+ = \alpha\alpha$	$T_+ = aa$
	$T_- = \beta\beta$	$T_o = \frac{1}{\sqrt{2}}(ab + ba)$
		$T_- = bb$

The wave function for the nuclear triplet is given by:

$$\Psi = c_0 \Phi_0 |S_0 T_0\rangle + c_v \tilde{\Phi}_v \times \left[|T_0 S_0\rangle + \left| \frac{1}{\sqrt{2}} (T_+ T_- - T_- T_+) \right\rangle \right] \quad (2.27)$$

and the corresponding energy is given by:

$$E = E_0 - \frac{\frac{1}{8} \left(q_{ov}^{(1)} - q_{ov}^{(2)} \right)^2}{E_v - E} - \frac{\frac{2}{8} \left(q_{ov}^{(1)} + q_{ov}^{(2)} \right)}{E_v - d - E} \quad (2.28)$$

Since $d \ll E_v$, $d \ll E$, Eq. 2.26 and 2.28 can be reduced:

$$E_{singlet} = E_0 - \frac{\frac{3}{8} \left(q_{ov}^{(1)} \right)^2}{E_v - E} + \frac{\frac{3}{4} q_{ov}^{(1)} q_{ov}^{(2)}}{E_v - E} - \frac{\frac{3}{8} \left(q_{ov}^{(2)} \right)^2}{E_v - E} \quad (2.29)$$

$$E_{triplet} = E_0 - \frac{\frac{3}{8} \left(q_{ov}^{(1)} \right)^2}{E_v - E} - \frac{\frac{1}{4} q_{ov}^{(1)} q_{ov}^{(2)}}{E_v - E} - \frac{\frac{3}{8} \left(q_{ov}^{(2)} \right)^2}{E_v - E} \quad (2.30)$$

Each of the coupling terms in Eq. 2.29 and 2.30 can be related to the coupling terms J_{11}, J_{22}, and J_{12} by considering the expression for the coupling energy derived from the point nucleus approximation for H_2 (two nuclei, with spin, but no electrons). The appropriate energy expression can be obtained by using an operator similar to that given for HD in Eq. 1.15, replacing H with H_1 and D with H_2, and by using nuclear spin functions appropriate to the hydrogen nucleus for both H_1 and H_2 (see Table 5). For the nuclear singlet, the energy is related to the coupling constants by the equation:

$$E_{singlet} = E_o + \tfrac{3}{4}hJ_{11} - \tfrac{3}{4}hJ_{12} + \tfrac{3}{4}hJ_{22} \quad (2.31)$$

Similarly, the nuclear triplet energy is related to the coupling constants by the equation:

$$E_{triplet} = E_o + \tfrac{3}{4}hJ_{11} + \tfrac{1}{4}hJ_{12} + \tfrac{3}{4}hJ_{22} \quad (2.32)$$

The total spin-spin coupling energy is given by the difference between the triplet and singlet energies. Consider the cross-term energy only:

$$\Delta E_{12} = E_{12(triplet)} - E_{12(singlet)} \quad (2.33)$$

From Eq. 2.29 and 2.30:

$$\Delta E = -\frac{q_{ov}^{(1)} q_{ov}^{(2)}}{E_v - E} = E_{3H_1H_2} \quad (2.34(a))$$

and from Eq. 2.31 and 2.32:

$$\Delta E_{12} = h J_{12} \qquad (2.34(b))$$

Thus the Fermi contact contribution to the coupling constant is given by:

$$J_{3H_1H_2} = \frac{- q_{ov}^{(1)} q_{ov}^{(2)}}{h(E_v - E)} \qquad (2.35)$$

J_{3HD} may be calculated using the same formula by substituting Q_D for Q_{H_2} into $q_{ov}^{(2)}$. Since J_{3HD} is positive, this implies that ϕ_v must be antisymmetric.

If $$q_{ov}^{\prime(1)} = q_{ov}^{(1)} / Q_{H_1} \qquad (2.36(a))$$

and $$q_{ov}^{\prime(2)} = q_{ov}^{(2)} / Q_{H_2} \qquad (2.36(b))$$

then $$q_{ov}^{\prime(1)} = -q_{ov}^{\prime(2)} \qquad (2.36(c))$$

Thus the expression for J_{3HD} becomes:

$$J_{3HD} = \frac{+ Q_H Q_D [q_{ov}^{\prime(1)}]^2}{h(E_v - E)} \qquad (2.37(a))$$

The coupling constant J_{3HD} was determined using three different sets of functions for Φ_o and $\tilde{\Phi}_v$. The first consisted of very simple LCAO/MO HD molecular wave functions:

$$\tilde{\Phi}_{tot\,1} = C_0 \left(\phi_0(1)\,\phi_0(2) \right) + C_V \frac{1}{N\sqrt{2}} \left(\phi_0(1)\,\phi_V(2) - \phi_V(1)\,\phi_0(2) \right) \tag{2.38}$$

where $$\phi_0 = N_0 \left(\frac{\epsilon^3}{\pi} \right)^{1/2} \left(e^{-\epsilon r_H} + e^{-\epsilon r_D} \right) \tag{2.38(a)}$$

$$\phi_V = N_V \left(\frac{\epsilon^3}{\pi} \right)^{1/2} \left(e^{-\epsilon r_H} - e^{-\epsilon r_D} \right) \tag{2.38(b)}$$

The second used the slightly more complex Coulson-Fischer wave function for $\tilde{\Phi}_0$:

$$\tilde{\Phi}_{tot\,2} = C_0 \left(\phi_0(1)\,\phi_0(2) - C_F\,\phi_V(1)\,\phi_V(2) \right) + C_V \frac{1}{N\sqrt{2}} \left(\phi_0(1)\,\phi_V(2) - \phi_V(1)\,\phi_0(2) \right) \tag{2.39}$$

where ϕ_0, ϕ_V are the same as in Eq. 2.38

This wave function introduces electron correlation into $\tilde{\Phi}_0$ via configuration interaction by introducing the ionic term $C_F\,\phi_V^{(1)}\,\phi_V^{(2)}$.[62,66] In the third case, the Coulson-Fischer function was again used for $\tilde{\Phi}_0$ but ϕ_0 and ϕ_V were "unlinked" so that their exponential scaling parameters were not necessarily the same:

$$\phi_0 = N_0 \left(\frac{\epsilon^3}{\pi} \right)^{1/2} \left(e^{-\epsilon r_H} + e^{-\epsilon r_D} \right) \tag{2.40(a)}$$

$$\phi_v = N_v \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} \left(e^{-\alpha r_H} - e^{-\alpha r_D}\right) \qquad (2.40(b))$$

For the Coulson-Fischer wave functions, the expression given for J_{3HD} is not quite correct. The one-electron integral $q'^{(1)}_{ov}$ is derived from the expansion of the two-electron integral:

$$\langle \Phi_o \mid \mathcal{H}_{3ns} \mid \tilde{\Phi}_v \rangle \qquad (2.41)$$

In the previous derivation:

$$\Phi_o = \phi_o(1)\,\phi_o(2) \qquad (2.25(a))$$

In the Coulson-Fischer derivation:

$$\Phi_o = \phi_o(1)\phi_o(2) - C_F \phi_v(1)\,\phi_v(2) \qquad (2.39(a))$$

The introduction of the C_F term yields the same integral, $q'^{(1)}_{ov}$, but it now must be multiplied by a factor of $(1 + C_F)$. As a result, the expression for J_{3HD} becomes:

$$J_{3HD} = \frac{+Q_H Q_D (1 + C_F)^2 \left[q'^{(1)}_{ov}\right]^2}{h(E_v - E)} \qquad (2.37(b))$$

The values of the exponential parameters in the three wave functions were determined by varying the ground state energy:

$$E_o = \langle \Phi_o \mathcal{H}_o \Phi_o \rangle \qquad (2.26(f))$$

with respect to ϵ (or ϵ and α in the third case). The resulting wave functions, energies, and parameters are given in Table 6 on page 90.

Since the parameters in $\tilde{\Phi}_v$ were determined by the parameters in Φ_o, no further minimization was necessary and J_{3HD} was determined directly using Eq. 2.37. In all calculations, the total energy E in the denominator was approximated by E_o since the ground state energy is much greater in magnitude than the coupling energies.

Two types of computer programmes were necessary to perform the required calculations:

1) Programmes to determine the ground state energy E_o and to minimize it with respect to the exponential parameters.

2) Programmes to calculate the coupling constant J_{3HD}.

1) The ground state energy was obtained by solving the integral:

$$E_o = \langle \Phi_o \mathcal{H}_o \Phi_o \rangle \qquad (2.26(f))$$

where for $\tilde{\Phi}_{tot\,1}$, $\Phi_o = \phi_o(1)\phi_o(2)$ (2.38)

for $\tilde{\Phi}_{tot\,2}$, $\tilde{\Phi}_{tot\,3}$

$$\Phi_o = \phi_o(1)\phi_o(2) - C_F \phi_v(1)\phi_v(2) \qquad (2.39)$$

For $\underset{\sim}{\Phi}_{\text{tot 1}}$, the integral 2.26(f) expands as follows:

$$E_o = \langle \phi_o(1)\phi_o(2) | \mathcal{H}_o | \phi_o(1)\phi_o(2) \rangle$$

$$= \langle \phi_o(2)\phi_o(2) \rangle \langle \phi_o(1) | -\frac{\nabla_1^2}{2} - \frac{1}{r_{1H}} - \frac{1}{r_{1D}} | \phi_o(1) \rangle$$

$$+ \langle \phi_o(1)\phi_o(1) \rangle \langle \phi_o(2) | -\frac{\nabla_2^2}{2} - \frac{1}{r_{2H}} - \frac{1}{r_{2D}} | \phi_o(2) \rangle$$

$$+ \langle \phi_o(1)\phi_o(2) | \frac{1}{r_{12}} | \phi_o(1)\phi_o(2) \rangle + \frac{1}{R}$$

$$= \Big\{ 2N_o^2 \frac{\epsilon^3}{\pi} \Big\langle (e^{-\epsilon r_H} + e^{-\epsilon r_D})$$

$$\Big| -\frac{\nabla_1^2}{2} - \frac{1}{r_H} - \frac{1}{r_D} \Big| (e^{-\epsilon r_H} + e^{-\epsilon r_D}) \Big\rangle$$

$$+ N_o^4 \frac{\epsilon^6}{\pi^2} \Big\langle (e^{-\epsilon r_{1H}} + e^{-\epsilon r_{1D}})(e^{-\epsilon r_{2H}} + e^{-\epsilon r_{2D}})$$

$$\Big| \frac{1}{r_{12}} \Big| (e^{-\epsilon r_{1H}} + e^{-\epsilon r_{1D}})(e^{-\epsilon r_{2H}} + e^{-\epsilon r_{2D}}) \Big\rangle$$

$$+ \frac{1}{R} \Big\}$$

(2.42)

The one-electron integral is simply $\mathcal{E}_o$, the one-electron hydrogen molecular energy calculated and programmed as outlined in Section 2.2. The two-electron integral is new. It can be expanded into a series of integrals having the form:

$$\left\langle \frac{1}{r_{12}} \left(e^{-\epsilon (r_{1N_1} + r_{2N_2} + r_{1N_3} + r_{2N_4})} \right) \right\rangle \tag{2.43}$$

where N_i = H or D (2.43(a))

The formulae for integrals of this form are given by Slater[62] in Chapters 3 and 4 and the derivations in Appendix 6. These were easily transformed into subroutines for the computer.

For $\tilde{\Phi}_{\text{tot } 2}$ and $\tilde{\Phi}_{\text{tot } 3}$, the integral 2.26(f) expands as follows:

$$\begin{aligned} E_o = & \langle \phi_o(1)\phi_o(2) - C_F \phi_v(1)\phi_v(2) \\ & | \mathcal{H}_o | \phi_o(1)\phi_o(2) - C_F \phi_v(1)\phi_v(2) \rangle \\ = & \langle \phi_o(1)\phi_o(2) | \mathcal{H}_o | \phi_o(1)\phi_o(2) \rangle \\ & + C_F^2 \langle \phi_v(1)\phi_v(2) | \mathcal{H}_o | \phi_v(1)\phi_v(2) \rangle \\ & - 2C_F \langle \phi_o(1)\phi_o(2) | \mathcal{H}_o | \phi_v(1)\phi_v(2) \rangle \end{aligned} \tag{2.44}$$

The first term is obviously the same as the E_o derived for $\tilde{\Phi}_{\text{tot 1}}$. For $\tilde{\Phi}_{\text{tot 2}}$, ϕ_v differs from ϕ_o only in symmetry:

$$\phi_o = N_o \left(\frac{\epsilon^3}{\pi}\right)^{1/2} \left(e^{-\epsilon r_H} + e^{-\epsilon r_D}\right) \qquad (2.38(a))$$

$$\phi_v = N_v \left(\frac{\epsilon^3}{\pi}\right)^{1/2} \left(e^{-\epsilon r_H} - e^{-\epsilon r_D}\right) \qquad (2.38(b))$$

Thus the expansion of the C_F^2 and C_F terms in Eq. 2.44 will result in the same types of integrals as the expansion of the first term, with the individual integrals in the summation differing only in sign. For example:

$$\left\langle \phi_o(1)\phi_o(2) \left| \frac{1}{r_{12}} \right| \phi_v(1)\phi_v(2) \right\rangle$$

$$= N_o^4 \frac{\epsilon^6}{\pi^2} \left\langle \left(e^{-\epsilon r_{1H}} + e^{-\epsilon r_{1D}}\right)\left(e^{-\epsilon_{2H}} + e^{-\epsilon r_{2D}}\right) \right.$$

$$\left. \left| \frac{1}{r_{12}} \right| \left(e^{-\epsilon r_{1H}} - e^{-\epsilon r_{1D}}\right)\left(e^{-\epsilon 2_H} - e^{-\epsilon 2_D}\right) \right\rangle$$

(2.45)

This can be compared with the $\frac{1}{r_{12}}$ term in Eq. 2.42, and it expands into terms of the sort given in Eq. 2.43.

For $\tilde{\Phi}_{\text{tot 3}}$, the C_F^2 term will be the same as the C_F^2 term in $\tilde{\Phi}_{\text{tot 2}}$ with all the parameters ϵ replaced by $\alpha \neq \epsilon$. The C_F term, however, is different:

$$-2C_F \langle \phi_o(1)\phi_o(2) | \mathcal{H}_o | \phi_v(1)\phi_v(2) \rangle$$

$$= -2C_F \left\{ 2N_o^2 \frac{(\epsilon\alpha)^{3/2}}{\pi} \left\langle (e^{-\epsilon r_H} + e^{-\epsilon r_D}) \left| -\frac{\nabla^2}{2} - \frac{1}{r_H} - \frac{1}{r_D} \right| (e^{-\alpha r_H} - e^{-\alpha r_D}) \right\rangle \right.$$

$$\left. + \frac{(\alpha\epsilon)^3}{\pi^2} \left\langle (e^{-\epsilon r_{1H}} + e^{-\epsilon r_{1D}})(e^{-\epsilon r_{2H}} + e^{-\epsilon r_{2D}}) \left| \frac{1}{r_{12}} \right| (e^{-\alpha r_{1H}} - e^{-\alpha r_{1D}})(e^{-\alpha r_{2H}} - e^{-\alpha r_{2D}}) \right\rangle \right\} \tag{2.46}$$

The first term can be expanded into a summation of one-electron integrals. Subroutines for these integrals were based upon the same formulae taken from Slater[62] (modified to fit two different scaling parameters) and McGlynn et al[65] as were used for the one-electron calculations. The second term is a two-electron integral which can be expanded into a summation of terms which have the form:

$$\left\langle \left(\frac{1}{r_{12}}\right) \left(e^{-\epsilon(r_{1N_1} + r_{2N_2}) - \alpha(r_{1N_3} + r_{2N_4})} \right) \right\rangle \tag{2.47}$$

where N_i = H or D (2.47(a))

The formulae given for two-electron integrals by Slater in Chapters 3 and 4 are not appropriate for wave functions containing two different scaling parameters. In some cases, the derivations given in Appendix 6 of Slater can be modified to give formulae for the two-parameter case. However, for some of the terms having the form given in 2.47, the derivations result in integrals which are not soluble analytically. Two possible recourses are available:

a) The use of recursion formulae

b) Transformation into a coordinate system in which the integrals are more easily soluble.

Recursion formulae adapt well to computer programming and may be applied to integrals of the type in Eq. 2.47, but if a wave function containing short-range terms (i.e., terms such as $r^n e^{-\kappa r}$) were to be considered in future calculations, difficulties would arise because the recursion formulae would contain terms such as $e^{+\kappa r}$ which are too large for the computer to handle. For this reason it was decided to use method (b). A subroutine based on such a method has been developed by Dingle.[51]

The programmes used to calculate E_o for all three wave functions required a variational subroutine to minimize E_o with respect to ϵ (in $\tilde{\Phi}_{tot\ 1}$ and $\tilde{\Phi}_{tot\ 2}$) or ϵ and α (in $\tilde{\Phi}_{tot\ 3}$). The minimization for $\tilde{\Phi}_{tot\ 3}$ required a two parameter procedure, and since the sections on the hydrogen

molecule in Slater's[62] and Coulson's[66] books supplied a check on the correct answers, the calculations did not require a highly efficient minimization routine such as the one based on Fibonacci search which was used in the one-electron, one-parameter calculations. For these reasons it was decided to use the internal programme MINFUN from the University of Victoria's Academic Systems Public Disk. The Coulson-Fischer calculations required an evaluation of the parameter C_F for each iteration, since its value depends upon the value of the scaling parameters.

2) A second programme calculated the coupling constant J_{3HD} using the formulae in Eq. 2.37(a) and 2.37(b). Since no minimization subroutine was necessary, the bulk of the programme was devoted to subroutines used in calculating E_v and $q'^{(1)}_{ov}$.

a) E_v. For all three wave functions, the triplet energy is given by:

$$E_v = \tfrac{1}{2} \langle \phi_o(1)\,\phi_v(2) - \phi_v(1)\,\phi_o(2) \,|\, \mathcal{H}_o \,|\, \phi_o(1)\,\phi_v(2) - \phi_v(1)\,\phi_o(2) \rangle$$

$$= \tfrac{1}{2} \{ \langle \phi_o(1)\phi_v(2) | \mathcal{H}_o | \phi_o(1)\phi_v(2) \rangle + \langle \phi_v(1)\phi_o(2) | \mathcal{H}_o | \phi_v(1)\phi_o(2) \rangle - 2\langle \phi_o(1)\phi_v(2) | \mathcal{H}_o | \phi_v(1)\phi_o(2) \rangle \}$$

$$= \left\langle \phi_o \left| -\frac{\nabla^2}{2} - \frac{1}{r_H} - \frac{1}{r_D} \right| \phi_o \right\rangle$$

$$+ \left\langle \phi_v \left| -\frac{\nabla^2}{2} - \frac{1}{r_H} - \frac{1}{r_D} \right| \phi_v \right\rangle$$

$$- \left\langle \phi_o(1)\phi_v(2) \left| \frac{1}{r_{12}} \right| \phi_v(1)\phi_o(2) \right\rangle$$

$$+ \frac{1}{2} \left\langle \phi_o(1)\phi_v(2) \left| \frac{1}{r_{12}} \right| \phi_o(1)\phi_v(2) \right\rangle$$

$$+ \frac{1}{2} \left\langle \phi_v(1)\phi_o(2) \left| \frac{1}{r_{12}} \right| \phi_v(1)\phi_o(2) \right\rangle$$

(2.48)

The first two terms are one-electron integrals which were required for the calculation of E_o. For the first two wave functions in which the parameter in ϕ_o has the same scaling parameter as ϕ_v, the formulae of Slater[62] were used without modification. In the third wave function, the scaling parameters differ, and both the overlap formulae of McGlynn et al[65] and those of Slater (modified) were used.

The last three terms are two-electron integrals. For the first two wave functions these integrals were calculated using the formulae in Slater directly since there was only one screening parameter, $\in$. For the third wave function these last three terms expand into integrals having

the form:

$$\left\langle \left(\frac{1}{r_{12}}\right)\left[e^{-(\epsilon r_{1N_1} + \alpha r_{2N_2} + \alpha r_{1N_3} + \epsilon r_{2N_4})}\right]\right\rangle \quad (2.49(a))$$

$$\left\langle \left(\frac{1}{r_{12}}\right)\left[e^{-(\epsilon r_{1N_1} + \alpha r_{2N_2} + \epsilon r_{1N_3} + \alpha r_{2N_4})}\right]\right\rangle \quad (2.49(b))$$

$$\left\langle \left(\frac{1}{r_{12}}\right)\left[e^{-(\alpha r_{1N_1} + \epsilon r_{2N_2} + \alpha r_{1N_3} + \epsilon r_{2N_4})}\right]\right\rangle \quad (2.49(c))$$

where N_i = H or D (2.49(d))

Formulae for some of these can be derived analytically using the methods outlined in Appendix 6 of Slater but for others this is not possible. For the latter integrals the calculations were accomplished using Dingle's two-electron integration subroutine.

b) $q_{ov}^{\prime(1)}$. For $\tilde{\Phi}_{\text{tot 1}}$ and $\tilde{\Phi}_{\text{tot 2}}$, the integral $q_{ov}^{\prime(1)}$ can be expanded as follows:

$$q_{ov}^{\prime(1)} = \langle \phi_o | Q_{11} | \phi_v \rangle$$

$$= N_o N_v \left(\frac{\epsilon^3}{\pi}\right)\left(\frac{K^3}{8\pi}\right)$$

$$\times \left\langle \left(e^{-\epsilon r_H} + e^{-\epsilon r_D}\right) \middle| e^{-K r_H} \middle| \left(e^{-\epsilon r_H} - e^{-\epsilon r_D}\right)\right\rangle \quad (2.50)$$

This integral is similar to the $\langle \tilde{\Phi}'_{1,H} | \omega_H(1) | \Phi_0 \rangle$ integral used in the one-electron calculations of J_{3HD} (it is, in fact, the same as the integral used in the long range calculations, if N_V is replaced by C_1), so the same subroutines were used for both. For $\tilde{\Phi}_{tot\ 3}$, $q'^{(1)}_{0V}$ expands into integrals in three different parameters:

$$q'^{(1)}_{0V} = \langle \phi_0 Q_{11} \phi_V \rangle$$

$$= N_0 N_V \frac{(\epsilon\alpha)^{3/2}}{\pi} \frac{K^3}{8\pi}$$

$$\times \langle (e^{-\epsilon r_H} + e^{-\epsilon r_D}) | e^{-K r_H} | (e^{-\alpha r_H} - e^{-\alpha r_D}) \rangle$$

$$= N_0 N_V \frac{(\epsilon\alpha)^{3/2}}{\pi} \frac{K^3}{8\pi} \left\{ \langle e^{-(\epsilon+K+\alpha) r_H} \rangle \right.$$

$$+ \langle e^{-[(K+\alpha) r_H + \epsilon r_D]} \rangle + \langle e^{-[(\epsilon+K) r_H + \alpha r_D]} \rangle$$

$$\left. + \langle e^{-[K r_H + (\epsilon+\alpha) r_D]} \rangle \right. \qquad (2.51)$$

The overlap formulae of McGlynn et al[65] were used to calculate the integrals in Eq. 2.51, but they had to be modified to cope with three different exponential parameters as well as with the large magnitude of K.

The results of the E_o calculations are given in Table 6 and the results of the J_{3HD} calculations are given in Table 7. Since for all three wave functions the scaling parameters were close to the same value ($\epsilon \simeq \alpha \simeq 1.2$), it

Table 6

Energies and Scaling Parameters for the Ground State Wave Function (Φ_o) used in the Calculation of J_{3HD}

Wave Function	E_o (Hartrees)	ϵ	α
tot 1	-1.128	1.19	-
tot 2	-1.148	1.20	-
tot 3	-1.148	1.20	1.19

Table 7

Comparison of J_{3HD} as Calculated using the Wave Functions in Section 2.2 (Two-electron Calculations)

Wave Function	J_{3HD} (Hz)	ϵ	α
tot 1	102.8	1.19	-
tot 2	127.6	1.20	-
tot 3	126.0	1.20	1.19

was decided to investigate the effect of varying the two parameters on the value of the coupling constant. Since the charge density at the nucleus depends upon the values of ϵ and α, the effect was expected to be large.

The electron density ρ_2 at the nucleus as described by $\tilde{\Phi}_{tot\ 2}$ is:

$$\rho_2 = \frac{\epsilon^3}{\pi}\left\{\frac{(1+e^{-2\epsilon R}+2e^{-\epsilon R})}{2(1+S(\epsilon R))}\right.$$

$$\left.+\frac{C_F^{\,2}(1+e^{-2\epsilon R}-2e^{-\epsilon R})}{2(1-S(\epsilon R)}-\frac{2C_F(1-e^{-2\epsilon R})}{2(1-S^2(\epsilon R))^{1/2}}\right\} \quad (2.52)$$

where $S(\epsilon R) = e^{-\epsilon R}\left(1+\epsilon R+\frac{(\epsilon R)^2}{3}\right)$ (2.52(a))

For $\Phi_{tot\ 3}$ the expression for ρ_3 is more complex:

$$\rho_3 = \frac{\epsilon^3}{\pi}\frac{(1+e^{-2\epsilon R}+2e^{-\epsilon R})}{2(1+S(\epsilon R))}$$

$$+\frac{\alpha^3}{\pi}C_F^{\,2}\frac{(1+e^{-2\alpha R}-2e^{-\alpha R})}{2(1-S(\alpha R))}$$

$$-\frac{(\alpha\epsilon)^{3/2}}{\pi}2C_F\frac{(1+e^{-\epsilon R}-e^{-\alpha R}-e^{-(\epsilon+\alpha)R})}{2(1+S(\epsilon R))^{1/2}(1-S(\alpha R))^{1/2}}$$

(2.53)

The densities calculated using these formulae with various values of ϵ and α (or ϵ alone for ρ_2) were matched against the optimum density of .2299.[60] The programme used to perform the density match for the two-electron case was

similar to that used for the corresponding one-electron case. For $\tilde{\Phi}_{\text{tot 3}}$, the density depends upon two scaling parameters, which effectively increases the number of iterations from n to n x n, so the accuracy was limited to ±.025. The results of the density match and the hetero-coupling constant calculated using the optimum parameters are given in Table 8. Note that, unlike the wave function used in the one-electron calculations (and unlike $\tilde{\Phi}_{\text{tot 1}}$, which would give a similar result), the parameters which give the best density at the nucleus are not the same as the parameters which give the best ground state energy. For $\tilde{\Phi}_{\text{tot 3}}$, the best density match was obtained for a combination in which $\epsilon > \alpha$ (1.48, 1.40). However, for some cases where $\alpha > \epsilon$, the match was almost as good. The (1.11, 1.31) combination was the best of these.

The parameter(s) in the trial wave function $\tilde{\Phi}_V$ for the preceding two-electron calculations were determined by their values in $\tilde{\Phi}_o$. A further calculation used a wave function $\tilde{\Phi}_{\text{tot 4}}$ in which $\tilde{\Phi}_V$ was not so linked to $\tilde{\Phi}_o$:

$$\tilde{\Phi}_{\text{tot 4}} = c_o \left(\phi_o(1)\,\phi_o(2)\right) + c_V\left(\phi_1(1)\,\phi_2(2) - \phi_2(1)\,\phi_1(2)\right) \qquad (2.54)$$

Table 8

J_{3HD} as Calculated using Scaling Parameters which provide an Optimum Electron Density Match at the Nucleus

Wave Function	J_{3HD} (Hz)	$\in$	α
$\tilde{\Phi}_{tot\ 2}$	106	1.36	-
$\tilde{\Phi}_{tot\ 3}$	148	1.48	1.40
$\tilde{\Phi}_{tot\ 3}$	98.0	1.11	1.31

Table 9

J_{3HD} as Calculated using $\tilde{\Phi}_{tot\ 4}$ (Variational Determination)

Parameter	Energy $(\tilde{E}^{(2)})$ (Hz)	J_{3HD} (Hz)
1.536 (optimum)	-1167 (minimum)	119.5
1.19	-1004	102.9

where $\phi_0 = N_0 \left(\frac{\epsilon^3}{\pi}\right)^{1/2} \left(e^{-\epsilon r_{H_1}} + e^{-\epsilon r_{H_2}}\right)$ (2.54(a))

$$\phi_1 = C_{1A} A + C_{1B} B \tag{2.54(b)}$$

$$\phi_2 = C_{2A} A + C_{2B} B \tag{2.54(c)}$$

$$A = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{H_1}} \tag{2.54(d)}$$

$$B = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{H_2}} \tag{2.54(e)}$$

If $\langle \phi_1 \phi_2 \rangle = 0$, then:

$$C_{1A} = C_{2B} \tag{2.54(f)}$$

$$C_{2A} = -C_{1B} \tag{2.54(g)}$$

so that $\tilde{\Phi}_V$ reduces to:

$$\begin{aligned} \tilde{\Phi}_V &= \frac{1}{\sqrt{2}} \left(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\right) \\ &= \frac{1}{\sqrt{2}} \left(C_{1A}^2 + C_{1B}^2\right)\left(A(1)B(2) - B(1)A(2)\right) \end{aligned} \tag{2.55}$$

If the wave function is normalized then:

$$C_{1A}^2 + C_{1B}^2 = \frac{1}{(1 - \sigma_{AB}^2)^{1/2}} \tag{2.56}$$

$$\sigma_{AB} = \int AB \, d\tau \tag{2.56(a)}$$

The formula for the total energy is given by:

$$E = E^{(0)} + \tilde{E}^{(2)}$$

$$= E_o - \frac{3}{(1-\sigma_{AB}^2)(E_v - E)}$$

$$\times \left\{ \tfrac{1}{8} \left(q_{oA}^{(1)} \sigma_{oB} - q_{oB}^{(1)} \sigma_{oA} \right)^2 \right.$$

$$+ \tfrac{1}{8} \left(q_{oA}^{(2)} \sigma_{oB} - q_{oB}^{(2)} \sigma_{oA} \right)^2$$

$$\left. - \tfrac{1}{4} \left(q_{oA}^{(1)} \sigma_{oB} - q_{oB}^{(1)} \sigma_{oA} \right) \left(q_{oA}^{(2)} \sigma_{oB} - q_{oB}^{(2)} \sigma_{oA} \right) \right\} \quad (2.57)$$

where $E_o = \langle \phi_o(1) \phi_o(2) | \mathcal{H}_o | \phi_o(1) \phi_o(2) \rangle$ (2.57(a))

$$E_v = \tfrac{1}{2} \langle (\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)$$

$$| \mathcal{H}_o | (\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) \rangle$$

$$= \tfrac{1}{2}(C_{1A}^2 + C_{1B}^2) \langle A(1)B(2) - B(1)A(2) | \mathcal{H}_o | A(1)B(2) - B(1)A(2) \rangle \quad (2.57(b))$$

$$q_{oA}^{(i)} = \langle \phi_o \, Q_{i1} \, A \rangle \quad (2.57(c))$$

$$q_{oB}^{(i)} = \langle \phi_o \, Q_{i1} \, B \rangle \quad (2.57(d))$$

$$\sigma_{oA} = \int \phi_o A \, d\tau \quad (2.57(e))$$

$$\sigma_{oB} = \int \phi_o B \, d\tau \quad (2.57(f))$$

An expression for J_{12} may be obtained from Eq. 2.57 by the same method that was used for the linked-parameter calculations:

$$J_{12} = \frac{1}{h(1-\sigma_{AB}^2)} \frac{(q_{oA}^{(1)}\sigma_{oB} - q_{oB}^{(1)}\sigma_{oA})(q_{oA}^{(2)}\sigma_{oB} - q_{oB}^{(2)}\sigma_{oA})}{E_V - E} \quad (2.58)$$

In order to calculate $J_{3HD'}$, deuteride must be substituted for the second hydrogen:

$$A' = e^{-\alpha r_H} \quad (2.59(a))$$

$$B' = e^{-\alpha r_D} \quad (2.59(b))$$

$$q_{oA'}^{(i)} = \frac{\langle \phi_o Q_{c_i} A' \rangle}{Q_{H_1}} \quad (2.59(c))$$

$$q_{oB'}^{(i)} = \frac{\langle \phi_o Q_{c_i} B' \rangle}{Q_{H_2}} \quad (2.59(d))$$

Since $E_o >> E^{(2)}$, $q_{oA'}^{(1)} = q_{oA'}^{(2)}$, $q_{oB'}^{(1)} = q_{oB'}^{(2)}$ and $\sigma_{oA'} = \sigma_{oB'}$, the equation for J_{3HD} reduces to:

$$J_{3HD} = \frac{Q_H Q_D \sigma_{oA'}^2}{h(1-\sigma_{A'B'}^2)} \frac{[q_{oA'}^{(1)} - q_{oB'}^{(1)}]^2}{E_V - E_o} \quad (2.60)$$

The E_o in Eq. 2.60 is the same as the E_o previously determined for calculations of J_{3HD} using $\tilde{\Phi}_{tot\,1}$. Inspection of Eq. 2.54, 2.55, and 2.56 and comparison to Eq. 2.38 and

2.39 shows that the trial wave functions $\tilde{\Phi}_V$ in $\tilde{\Phi}_{tot1}$ and $\tilde{\Phi}_{tot2}$ differ only in the scaling parameter ϵ from the trial wave function $\tilde{\Phi}_V$ in $\tilde{\Phi}_{tot4}$. Thus E_V for $\tilde{\Phi}_{tot4}$ can be calculated using the same equations for E_V as derived for $\tilde{\Phi}_{tot1}$ and $\tilde{\Phi}_{tot2}$ by simply replacing the scaling parameter α for ϵ. Since the same formula for E_V was used for three of the four wave functions used in the two-electron calculations of J_{3HD}, it provided a good "checkpoint" for the accuracy of the calculations. The trial wave function $\tilde{\Phi}_V$ in all three cases corresponds to the $^3\Sigma_\mu, M_S = 0$ state of H_2 as documented by Slater[62] in Table 4-1. His Figure 4-1 provides a graph of molecular energy versus the internuclear distance R for the case where ϵ or α in $\tilde{\Phi}_V$ is equal to 1. Using values of R = 1 and R = 2 (the value of R = 1.4 used in the calculations of J_{3HD} could not be read accurately from the graph), E_V calculated using the formula derived in this section attained values of -.29 Hartrees and -.85 Hartrees, respectively. These results agree well with those of Slater.

The integral $q_{0A'}^{(1)}$ can be expanded to yield:

$$q_{0A'}^{(1)} = \langle \phi_0 Q_{11} A' \rangle$$

$$= N_0 \frac{(\epsilon\alpha)^{3/2}}{\pi} \frac{K^3}{8} \langle e^{-(\epsilon r_{1A} + \epsilon r_{01})} | e^{-Kr_H} | e^{-\alpha r_H} \rangle \qquad (2.61)$$

and $q_{oB'}^{(1)}$ can be similarly expanded:

$$q_{oB'}^{(1)} = \langle \phi_o \, Q_{11} \, B' \rangle$$

$$= N_o \frac{(\epsilon\alpha)^{3/2}}{\pi} \frac{K^3}{8\pi} \left\langle e^{-(\epsilon r_A + \epsilon r_B)} \middle| e^{-Kr_A} \middle| e^{-\alpha r_B} \right\rangle \quad (2.62)$$

These integrals are obviously similar to the integral $q_{ov'}^{(1)}$ used in calculating J_{3HD} with $\tilde{\Phi}_{tot\,3}$ (see Eq. 2.51) and the same overlap subroutines were used for both.

Since $\tilde{\Phi}_v$ is not linked to $\tilde{\Phi}_o$ via its scaling parameter, the total energy as given in Eq. 2.57 can be minimized with respect to the parameter α in $\tilde{\Phi}_v$. The value of E_o is much greater than the value of $E^{(2)}$, but the ground state energy is not affected by the value of α so it is only necessary to minimize the second order term. In the computer programme used for the $\tilde{\Phi}_{tot\,4}$ calculation of J_{3HD}, the internal subroutine MINFUN was used to minimize $\tilde{E}^{(2)}$ with respect to α. The optimum value of α, along with the minimized energy and hetero-coupling constant, are given in Table 9. In addition, the coupling constant has been calculated using a value of 1.19 for α in order to compare the results for $\tilde{\Phi}_{tot\,1}$ and $\tilde{\Phi}_{tot\,4}$. These results should be the same since at $\alpha = \epsilon = 1.19$ the wave functions are the same. Within the margin of error, they do, in fact, agree.

The results for the two-electron calculations of

J_{3HD} are obviously not very good, since comparison with the experimental value of 39 Hz demonstrates that they are two and a half to three times too large. Moreover, the results for $\tilde{\Phi}_{tot2}$ and $\tilde{\Phi}_{tot3}$, in which some electron correlation was introduced into the ground state wave function, and for $\tilde{\Phi}_{tot4}$, for which the second-order energy was minimized with respect to the scaling parameter in the trial (triplet) wave function, are worse than for the relatively simple $\tilde{\Phi}_{tot1}$. There are two possible reasons for these unimpressive results, both of which concern the form of the trial (triplet) wave function.

1) In the derivations of the formulae for $\tilde{E}^{(2)}$ and J_{3HD} which have been described in Section 2.2, the trial (triplet) wave function was assumed to have the form:

$$\tilde{\Phi}_v = \frac{1}{\sqrt{2}} \left(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2) \right)$$

(2.25) and (2.54)

where ϕ_1 is a symmetric wave function and is <u>either</u> symmetric or antisymmetric, but was assumed to be antisymmetric to give the correct sign for J_{3HD}.

Further analysis indicates that the triplet wave function should, in fact, be composed of both a symmetric and an

antisymmetric part:

$$\tilde{\Phi}_v = C_+ \Phi_+ + C_- \Phi_- \qquad (2.63)$$

where

$$\Phi_\pm = \frac{1}{N\sqrt{2}}\left(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\right) \qquad (2.63(a))$$

such that ϕ_1 is symmetric in both Φ_+ and Φ_- and ϕ_2 is symmetric in Φ_+ and antisymmetric in Φ_-. Obviously if ϕ_2 is symmetric it cannot have the same scaling parameter as ϕ_1.

2) The one-electron calculations gave good results when a triplet wave function constructed of long-range terms only was used as the trial function. It may be, however, that this is only true for the one-electron derivation presented in Section 2.1, in which the short-range terms cancel out and the long-range terms are related in such a way that the long range expression for E_{3HD} automatically yields the correct value. Further analysis indicates that short-range interactions should, in fact, contribute to the spin-spin coupling in the more general two-electron case and that the trial wave function should contain some short-range terms.

Both of these suggestions are discussed more fully in Chapter 3.

CHAPTER 3

DISCUSSION

It was suggested at the end of Chapter 2 that the form of the total spatial part of the wave function should be:

$$\tilde{\Phi}_{tot} = C_0 \Phi_0 + C_+ \Phi_+ + C_- \Phi_- \qquad (3.1)$$

where $\Phi_0 = \phi_0(1)\,\phi_0(2)$ (3.1(a))

$$\Phi_\pm = \frac{1}{\sqrt{2}}\left[\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\right] \qquad (3.1(b))$$

such that the ϕ_0 are symmetric, ϕ_1 is symmetric, and ϕ_2 is symmetric in Φ_+ but antisymmetric in Φ_-. The case where $\phi_2(2)$ is antisymmetric corresponds to the wave functions used in the two-electron calculations in Section 2.2.

C_0 is related to C_+ and C_- by:

$$C_0 = \sqrt{1 + C_+^2 + C_-^2} \qquad (3.1(c))$$

$$\simeq 1 + \frac{C_+^2}{2} - \frac{C_-^2}{2}$$

The effect of including the symmetric term $C_+ \overline{\Phi}_+$ in the wave function can best be studied by deriving an expression for the total energy. The one-electron calculations in Chapter 2 were based on energy expressions derived using an isotropic operator while the two-electron calculations were based on energy expressions derived using an anisotropic operator. It can be shown that both the isotropic and anisotropic operators will eventually give the same relationships, but it is much easier to use the isotropic operator in the derivations. In the following analysis, the magnetic field is assumed to be polarized along the z-axis of the molecule so that the operator is given by:

$$\mathcal{H}_{ns}' = \hat{Q}_{11}\hat{S}_{1z}\cdot\hat{I}_{1z} + \hat{Q}_{21}\hat{S}_{1z}\cdot\hat{I}_{2z} + \hat{Q}_{12}\hat{S}_{2z}\cdot\hat{I}_{1z} + Q_{22}\hat{S}_{2z}\cdot\hat{I}_{2z} \tag{3.2}$$

where (3.2(a))

$$\hat{Q}_{ji} = \frac{\lambda_j K^3 e^{-Kr_{ij}}}{8} \quad \text{where } \lambda_j = \frac{Q_j}{\pi}$$

or $$\hat{Q}_{ji} = \frac{\lambda_j K^2 e^{-Kr_{ij}}}{4r_{ij}} \tag{3.2(b)}$$

It is assumed that there are two different nuclei, both with spin of ½ so that $\lambda_i \neq \lambda_j$ for $i \neq j$.

The general expression for the total energy (spin-spin coupling energy added to the electronic energy which

accounts for most of the energy in the molecule) is similar to the one given in Eq. 2.22:

$$E = \langle \psi_0 + \tilde{\psi}_1 | \mathcal{H}_0 + \mathcal{H}_{ns}' | \psi_0 + \tilde{\psi}_1 \rangle \qquad (3.3)$$

where $\psi_0 = c_0 \Phi_0 \times$ electronic spin function x nuclear spin function (3.3(a))

$\tilde{\psi}_1 = (c_+ \Phi_+ + c_- \Phi_-)$ x electronic spin function x nuclear spin function (3.3(b))

and $\int (\psi_0 + \tilde{\psi}_1)(\psi_0 + \tilde{\psi}_1) d\tau = 1$ (3.3(c))

For the system described above, where $m = \pm \frac{1}{2}$, the electronic and nuclear spin functions are the same as those given in Table 5 (see Chapter 2). The operator $\mathcal{H}_{ns}'$ acts upon the spin functions in such a way that coupling is only non-zero between states which have opposing symmetries in their electronic spin functions. Equation 3.3 can be written in the form of a determinant:

	Φ_0	Φ_+	Φ_-
Φ_0	$E_0 - E$	H_{0+}'	H_{0-}'
Φ_+	H_{0+}'	$E_+ - E$	0
Φ_-	H_{0-}'	0	$E_- - E$

(3.4)

where $H_{o+}' = \langle \Phi_o | \mathcal{H}_{ns} | \Phi_+ \rangle$ (3.4(a))

$$H_{o-}' = \langle \Phi_o | \mathcal{H}_{ns} | \Phi_- \rangle \quad (3.4(b))$$

$$E_o = \langle \Phi_o | \mathcal{H}_o | \Phi_o \rangle \quad (3.4(c))$$

$$E_+ = \langle \Phi_+ | \mathcal{H}_o | \Phi_+ \rangle \quad (3.4(d))$$

$$E_- = \langle \Phi_- | \mathcal{H}_o | \Phi_- \rangle \quad (3.4(e))$$

The other possible terms are equal to zero by either symmetry or spin:

$$H_{+-}^{\circ} = \langle \Phi_+ | \mathcal{H}_o | \Phi_- \rangle \quad (3.4(f))$$

$$H_{++}' = \langle \Phi_+ | \mathcal{H}_{ns} | \Phi_+ \rangle \quad (3.4(g))$$

$$H_{--}' = \langle \Phi_- | \mathcal{H}_{ns} | \Phi_- \rangle \quad (3.4(h))$$

$$H_{oo}' = \langle \Phi_o | \mathcal{H}_{ns} | \Phi_o \rangle \quad (3.4(i))$$

$$H_{o+}^{\circ} = \langle \Phi_o | \mathcal{H}_o | \Phi_+ \rangle \quad (3.4(j))$$

$$H_{o-}^{\circ} = \langle \Phi_o | \mathcal{H}_o | \Phi_- \rangle \quad (3.4(k))$$

$$H_{+-}' = \langle \Phi_+ | 2\mathcal{H}_{ns} | \Phi_- \rangle \qquad (3.4(1))$$

$$= 0$$

Expanding the determinant and solving for E reduces the determinant to a relatively simpler equation:

$$E = E_o - \frac{(H_{+o}')^2}{E_+ - E} - \frac{(H_{-o}')^2}{E_- - E} \qquad (3.5)$$

For the case where the nuclear spins are parallel to each other then:

$$H_{\pm o}' = \langle \Phi_o | \tfrac{1}{4}(Q_{11} - Q_{12} + Q_{21} - Q_{22}) | \Phi_\pm \rangle \qquad (3.6(a))$$

Since $\Phi_\pm$ are antisymmetric with respect to electron exchange and Φ_o is symmetric:

$$\langle \Phi_o | Q_{j1} | \Phi_\pm \rangle = - \langle \Phi_o | Q_{j2} | \Phi_\pm \rangle \qquad (3.6(b))$$

$$\therefore \quad H_{\pm o} = \tfrac{1}{2} \langle \Phi_o | Q_{11} + Q_{21} | \Phi_\pm \rangle \qquad (3.6(c))$$

Now take:

$$\langle \Phi_0 | Q_{j1} | \Phi_\pm \rangle = \lambda_j \langle \Phi_0 | Q_{11}^{\ 0} | \Phi_\pm \rangle \qquad (3.6(d))$$

Then using the spatial symmetry of Φ_+ and Φ_- :

$$\lambda_2 \langle \Phi_0 | Q_{21}^{\ 0} | \Phi_\pm \rangle = \pm \lambda_2 \langle \Phi_0 | Q_{11}^{\ 0} | \Phi_\pm \rangle \qquad (3.6(e))$$

$$\therefore \quad H_{\pm 0} = \frac{\lambda_1 \pm \lambda_2}{2} \langle \Phi_0 | Q_{11}^{\ 0} | \Phi_\pm \rangle = \frac{\lambda_1 \pm \lambda_2}{2} Q_{11}^{\pm 0} \qquad (3.6(f))$$

Substituting Eq. 3.6(f) into Eq. 3.5 reformulates the equation in terms of the integral $Q_{11}^{\pm 0}$:

$$E_{rr} = E_0 - \frac{(\lambda_1^2 + \lambda_2^2)}{4} \left\{ \frac{(Q_{11}^{+0})^2}{E_+ - E} + \frac{(Q_{11}^{-0})^2}{E_- - E} \right\}$$

$$- \frac{\lambda_1 \lambda_2}{2} \left\{ \frac{(Q_{11}^{+0})^2}{E_+ - E} - \frac{(Q_{11}^{-0})^2}{E_- - E} \right\} \qquad (3.7)$$

Similarly for the case where the nuclear spins are anti-parallel:

$$H'_{\pm 0} = \langle \Phi_0 | \tfrac{1}{4}(Q_{11} - Q_{12} - Q_{21} + Q_{22} | \Phi_\pm \rangle \qquad (3.8(a))$$

$$= \langle \Phi_0 | Q_{11} - Q_{21} | \Phi_\pm \rangle \qquad (3.8(b))$$

$$= \frac{\lambda_1 \mp \lambda_2}{2} \langle \Phi_0 | Q_{11}^{0} | \Phi_\pm \rangle = \frac{\lambda_1 \mp \lambda_2}{2} Q_{11}^{\pm 0} \quad (3.8(c))$$

so that:

$$E_{\uparrow\downarrow} = E_0 - \frac{(\lambda_1^2 + \lambda_2^2)}{4} \left\{ \frac{(Q_{11}^{+0})^2}{E_+ - E} + \frac{(Q_{11}^{-0})^2}{E_- - E} \right.$$

$$\left. + \frac{\lambda_1 \lambda_2}{2} \left\{ \frac{(Q_{11}^{+0})^2}{E_+ - E} - \frac{(Q_{11}^{-0})^2}{E_- - E} \right\} \right. \quad (3.9)$$

For the isotropic case (presence of a polarizing nuclear field):

$$E_{\uparrow\uparrow} = + \frac{1}{4} J_{12\uparrow\uparrow} \quad (3.10(a))$$

$$E_{\uparrow\downarrow} = - \frac{1}{4} J_{12\uparrow\downarrow} \quad (3.10(b))$$

(Note that $E_{\uparrow\downarrow}$ is not the same as $E_{\uparrow\downarrow}$ for the anisotropic case in which $E_{\uparrow\downarrow} = -3/4\ J_{12}$.) Taking the difference between Eq. 3.10(a) and 3.10(b) and equating it to the difference between Eq. 3.7 and 3.9 yields an expression for J_{12}:

$$J_{12} = \frac{2\,\Delta E_{12}}{h} = - \frac{2 \lambda_1 \lambda_2}{h} \left\{ \frac{(Q_{11}^{+0})^2}{E_+ - E} - \frac{(Q_{11}^{-0})^2}{E_- - E} \right\} \quad (3.11)$$

In the two-electron derivation of J_{12} as described in Section 2.2, $Q_{11}^{+0} = 0$ and $\lambda_1 - \lambda_2 = 0$, i.e. $\lambda_1 = \lambda_2$

The expression for J_{12} under these conditions reduces to:

$$J_{12} = \frac{2\Delta E_{12}}{h} = \frac{2Q_H^2 (Q_{11}^{-0})^2}{h(E_- - E)} \tag{3.12}$$

$$= \frac{Q_H^2 (q_{0-})^2}{h(E_- - E)}$$

where $q_{0-} = \langle \phi_0 Q_{11}^{-0} \phi_{2-} \rangle$ (3.12(a))

This agrees with Eq. 2.37(a) (the equation for J_{3HD}) if one of the Q_H's is replaced by Q_D. However, neglect of the symmetric contribution to $\tilde{\Phi}_r$ may not be valid. If the expression for J_{12} is expanded in terms of one-electron integrals then:

$$(Q_{11}^{+0})^2 = \tfrac{1}{2} (q_{0+} - q_{00}\sigma_{0+})^2 \tag{3.13}$$

where $q_{0+} = \langle \phi_0 Q_{11}^{+0} \phi_{2+} \rangle$ (3.13(a))

$$q_{00} = \langle \phi_0 Q_{11}^{+0} \phi_0 \rangle \tag{3.13(b)}$$

$$\sigma_{0+} = \langle \phi_0 \phi_{2+} \rangle \tag{3.13(c)}$$

$$(Q_{11}^{-0})^2 = \tfrac{1}{2} (q_{p-})^2 \tag{3.14}$$

The $q_{00}\sigma_{0-}$ term is zero because ϕ_0 is symmetric while ϕ_{2-} is antisymmetric.

$$J_{12} = -\lambda_1\lambda_2\left\{\frac{(q_{0+} - q_{00}\sigma_{0+})^2}{E_+ - E} - \frac{(q_{0-})^2}{E_- - E}\right\} \tag{3.15}$$

$$= -\lambda_1\lambda_2\left\{\frac{q_{0+}^2 - 2q_{0+}q_{00}\sigma_{0+} + q_{00}^2\sigma_{0+}^2}{E_+ - E} - \frac{(q_{0-})^2}{E_- - E}\right\}$$

Now suppose the trial (triplet) wave function is dominated by some term which is sharply peaked at the nucleus. Both of the triplet energies E_+ and E_- will then be dominated by the kinetic energy term which will be very large due to the short range contribution, so that $E_+ \approx E_-$. Also, q_{0+} will be approximately equal to q_{0-}. The $q_{0\pm}^2$ terms in Eq. 3.15 will then cancel each other so that:

$$J_{12} = \lambda_1\lambda_2\frac{(2q_{0+}q_{00}\sigma_{0+} - q_{00}^2\sigma_{0+}^2)}{E_+ - E} \tag{3.16}$$

Since q_{00} is very small, the dominant term in J_{12} will be $2\,q_{0+}\,q_{00}\,\sigma_{0+}$. This is not, however, true of the self-coupling energies. The self-coupling terms are proportional to:

$$\frac{(Q_{11}^{+0})^2}{E_+ - E} + \frac{(Q_{11}^{-0})^2}{E_- - E} \tag{3.17}$$

If these terms are expanded under the assumption that the triplet wave function is dominated by a peaked short-range term, the $(q_{\pm o})^2$ terms are additive and contribute the largest portion of the energy. Since $q_{\pm o} >> q_{oo}\, \sigma_{o+}$, the self-coupling energies will be much larger than the cross-coupling energies. This suggests that the trial wave function should be determined by doing a variational calculation on the self-coupling energy, and the result then used to calculate the cross-coupling energy directly.

The question should then be asked: what form of trial wave function will give a reasonable self-coupling energy? The desirable wave function should have both a short-range and a long-range contribution. In the first set of calculations for the one-electron approximation, the trial function contained both short and long-range terms:

$$\tilde{\varphi}_1^H = C_1 e^{-\sigma r_H} + C_2 e^{-\sigma r_D} + \tilde{C}_H e^{-\kappa r_H} \qquad (2.10(b))$$

and the analogous two-electron functions would be:

$$\varphi_{1\pm} = C_1 (e^{-\frac{1}{2}\gamma r_H} + e^{-\frac{1}{2}\gamma r_D}) + C_2 (e^{-\kappa r_H} + e^{-\kappa r_D}) \qquad (3.18(a))$$

$$(\tfrac{1}{2}\gamma \cong \epsilon)$$

$$\phi_{2+} = C_1^+ \left(e^{-\alpha r_H} + e^{-\alpha r_D}\right) + C_2^+ \left(e^{-Kr_H} + e^{-Kr_D}\right) \qquad (3.18(b))$$

$$\phi_{2-} = C_1^+ \left(e^{-\alpha r_H} - e^{-\alpha r_D}\right) + C_2^- \left(e^{-Kr_H} - e^{-Kr_D}\right) \qquad (3.18(c))$$

$(\alpha \cong 1)$

However, this may not be the best form of the wave function to use. The first-order wave function obtained for hyperfine splitting in the H-atom using the operator $V_1(r)$ in Eq. 1.57 (i.e. Eq. 3.2(a)) is:

$$\phi_1^{1s}(r) = \frac{e^{-r}}{\sqrt{\pi}} \frac{Q_H K^3}{\pi (K+2)^3} \left\{ [E_1(Kr) + \ln Kr + \gamma] + r + D - \frac{(1-e^{-Kr})}{2r} + \frac{(K+2)^2 e^{-Kr}}{4K} \right\} \qquad (3.19)$$

where

$$D = -\frac{5}{2} - \ln \frac{K+2}{2} \quad \text{if } \langle \phi_1^{1s} \phi_0^{1s} \rangle = 0 \qquad (3.19(a))$$

and the corresponding second order energy is:

$$E^{(2)} = \frac{Q_H^2}{\pi^2} \frac{K^6}{(K+2)^6} \left[\frac{-5K}{32} - \frac{51}{32} + \ln \frac{4(K+1)}{(K+2)^2} + \frac{3}{4K} - \frac{9}{16(K+1)} + \frac{3}{K+2} + \frac{1}{16(K+1)^2} + \frac{5}{32K(K+1)} + \frac{1}{32K(K+1)^2} \right] \qquad (3.20)$$

For the operator $V_2(r)$ (see Eq. 3.2(b)) the equations are

similar:

$$\phi_1^{1s}(r) = \frac{e^{-r}}{\sqrt{\pi}} \frac{Q_H}{\pi} \frac{K^2}{(K+2)^2} \left\{ [E_1(-Kr) + \ln r + \gamma] + r + D - \frac{(1-e^{-Kr})}{2r} \right\} \tag{3.21}$$

where

$$D = -\frac{5}{2} - \ln \frac{(K+2)}{2} + \frac{2}{K+2} \tag{3.21(a)}$$

$$\text{if } \langle \phi_1^{1s} \phi_0^{1s} \rangle = 0$$

The corresponding second order energy is:

$$E^{(2)} = -\frac{Q_H^2}{\pi^2} \frac{K^4}{(K+2)^4} \left[\frac{K}{4} + \frac{9}{4} + \ln \frac{(K+2)^2}{4(K+1)} - \frac{4}{K+2} + \frac{1}{4(K+1)} \right] \tag{3.22}$$

The second order energy is of the order of magnitude of Q_H^2/π^2 so only the terms $\frac{-5}{32}$ - $\frac{51}{32}$ in Eq. 3.20 and $\frac{K}{4} + \frac{9}{4}$ in Eq. 3.22 contribute significantly. In both cases the part of the first order wave function that gives rise to these terms is the $\left(\frac{1-e^{-Kr}}{2r}\right)\left(\frac{e^{-r}}{\sqrt{\pi}}\right)$ term.

A reasonable trial wave function for spin-spin-coupling in HD based on this type of term would be:

$$\phi_1 = N_\gamma \left(\frac{}{\pi}\right)^{3/2} \left(e^{-\frac{1}{2}r_H} + e^{-\frac{1}{2}r_D}\right)$$

$$\tfrac{1}{2} \approx \epsilon \text{ in } \phi_0 \tag{3.23(a)}$$

$$\phi_2^{\pm} = C_1^{\pm}\left(\frac{e^{-\alpha r_H}}{r_H} \pm \frac{e^{-\alpha r_D}}{r_D}\right) - C_2^{\pm}\left(\frac{e^{-\beta r_H}}{r_H} \pm \frac{e^{-\beta r_D}}{r_D}\right) \qquad (3.23(b))$$

where α is of the order of magnitude of 10^0 and $\beta = K_1 + \alpha$ is of the order of magnitude of 10^{+5}. The parameters α and β can be varied to give an optimum value for the self-coupling energy, and the wave function with the optimized parameters then used to calculate J_{3HD}. Preliminary, approximate calculations indicate that a wave function like the one in Eq. 3.23 with $\alpha = 1$ and $\beta = 30000 + 1$ should lead to heterocoupling constants of the order of magnitude of Q^2/π^2 which is correct. In contrast, a wave function without the $\frac{1}{r_N}$ dependence (see Eq. 3.18) appears to lead to coupling constants which are too large. While both wave functions are peaked at the nucleus, the function which is dependent on $\frac{1}{r_N}$ falls off faster as distance from the nucleus increases, indicating that the short range contribution is only important very close to the nucleus.

The wave function proposed in Eq. 3.23 will probably result in self - coupling energies which are too large and hence unphysical. However, this feature results from spurious terms introduced by the form of the operator. In the expression for the self-coupling energy, these

terms are significant, but it is possible that they cancel in the calculation of J_{3HD}. Detailed calculations for HD using such a wave function have not yet been attempted. Such calculations must test the tentative conclusions that:

1) The trial (triplet) wave function must consist of both a symmetric and an antisymmetric part.

2) The trial wave function must contain both short-range and long-range contributions.

3) The trial wavefunction should be based on terms similar to those which give the main contribution to the hyperfine splitting energy in the H-atom. It is possible that, in a molecule, other long-range terms such as $\frac{re^{-r}}{\sqrt{\pi}}$ and $\frac{e^{-r}}{\sqrt{\pi}\,r}$ may also contribute to the heterocoupling energy and this should be examined.

4) A variational calculation of the self-coupling energy with respect to the short and long-range scaling parameters β and α could lead to results which are too large. However, the optimized wave function can still be used to calculate J_{3HD} if the unphysical terms cancel in the equation for the cross-coupling energy.

If the $\frac{e^{-\alpha r} - e^{-\beta r}}{r}$ type term does provide the main contribution to the self and cross-coupling energies, the trial wave function for spin-spin coupling

between hydrogen atoms in any molecule could likely be based on this type of term. The major part of the calculation would then consist of finding an appropriate ground state wave function. Such a situation is obviously desirable, but its testing must wait for the future.

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APPENDIX 1

A Few Notes on Basic Perturbation Theory and the Perturbation-Variation Method

Perturbation theory assumes that the total system described by the Schrodinger Equation:

$$\mathcal{H}\psi = E\psi \qquad \text{Al.1}$$

may be represented by the sum of a Hamiltonian $\mathcal{H}_o$ for some system for which the solution, $\psi^{(0)}$, is known (usually $\mathcal{H}_o$ is the non-relativistic electronic Hamiltonian) and some perturbation operators $\mathcal{H}_r'$ such that:

$$\mathcal{H}(\lambda) = \mathcal{H}_o + \sum_r \lambda_r \mathcal{H}_r' \qquad \text{Al.2}$$

where $$\mathcal{H}_o \psi^{(o)} = E^{(o)} \psi^{(o)} \qquad \text{Al.3}$$

is the zeroth order (unperturbed) Schrodinger Equation and the λ_r are strength parameters which measure the contribution from each perturbation.

To solve Al.2 it is assumed that the total wave function and total energy may be expressed in terms of the zeroth order wave functions, $\psi_k^{(0)}$, and eigenvalues, $E^{(0)}$, and the appropriate number of nth order perturbation functions and energies. These may be written as a Taylor series expansion in the λ_r:

$$E(\lambda) = E^{(0)} + \sum_r \lambda_r \left(\frac{\partial E(\lambda)}{\partial \lambda_r}\right)_0 + \frac{1}{2}\sum_r \sum_s \lambda_r \lambda_s \left(\frac{\partial^2 E(\lambda)}{\partial \lambda_r \partial \lambda_s}\right)_0 + \ldots$$

$$= E^{(0)} + \sum_r \lambda_r E_r^{(1)} + \frac{1}{2}\sum_r \sum_s \lambda_r \lambda_s E_{rs}^{(2)} + \ldots \quad \text{Al.4(a)}$$

$$\psi(\lambda) = \psi^{(0)} + \sum_r \left(\frac{\partial \psi(\lambda)}{\partial \lambda_r}\right)_0 + \frac{1}{2}\sum_r \sum_s \lambda_r \lambda_s \left(\frac{\partial^2 \psi(\lambda)}{\partial \lambda_r \partial \lambda_s}\right)_0 + \ldots$$

$$= \psi^{(0)} + \sum_r \lambda_r \psi_r^{(1)} + \frac{1}{2}\sum_r \sum_s \psi_{rs}^{(2)} + \ldots \quad \text{Al.5(a)}$$

For a single perturbation $\lambda \mathcal{H}'$, equations Al.4(a) and Al.5(a) reduce to:

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \quad \text{Al.4(b)}$$

$$\psi(\lambda) = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots \quad \text{Al.5(b)}$$

and the Schrodinger Equation may be written as:

$$(\mathcal{H}_0 + \lambda \mathcal{H}')(\psi^{(0)} + \lambda \psi^{(1)} + \ldots) = (E^{(0)} + \lambda E^{(1)} + \ldots)(\psi^{(0)} + \lambda \psi^{(1)} + \ldots) \quad \text{Al.6}$$

Collecting terms common in powers of λ yields the following expression:

$$(\mathcal{H}_0 \psi^{(0)} - E^{(0)} \psi^{(0)}) + \sum_{s=1}^{\infty} \lambda^s \left(- \sum_{t=0}^{s} E^{(t-s)} \psi^{(t)} + \mathcal{H}_0 \psi^{(s)} + \mathcal{H}' \psi^{(s-1)} \right) = 0 \qquad \text{Al.7}$$

If this equation is to be independent of λ, then the bracketed expressions must equal zero; thus the solution of Al.7 reduces to a set of s + 1 differential equations:

$$(\mathcal{H}_0 - E^{(0)}) \psi^{(0)} = 0 \qquad \text{Al.8(a)}$$

$$(\mathcal{H}_0 - E^{(0)}) \psi^{(1)} + (\mathcal{H}' - E^{(1)}) \psi^{(0)} = 0 \qquad \text{Al.8(b)}$$

$$(\mathcal{H}_0 - E^{(0)}) \psi^{(2)} + (\mathcal{H}' - E^{(1)}) \psi^{(1)} - E^{(2)} \psi^{(0)} = 0 \qquad \text{Al.8(c)}$$

$$\vdots$$

The first order energy can be calculated from Al.8(a) and Al.8(b) and requires only the zeroth order wave function and the perturbation operator provided $\psi^{(1)}$ is defined on the same space as $\psi^{(0)}$ and $\mathcal{H}_0$ is Hermitian:

$$E^{(1)} = \frac{\langle \psi^{(0)} \mathcal{H}' \psi^{(0)} \rangle}{\langle \psi^{(0)} \psi^{(0)} \rangle} \qquad \text{Al.9}$$

If $\psi^{(0)}$ is normalized, the denominator reduces to unity.

Properties such as spin-spin coupling which require second order or higher energies cannot be calculated unless first or even higher order wave functions are known since

from A1.8(a), A1.8(b), and A1.8(c):

$$E^{(2)} = \langle \psi^{(0)} \mathcal{H}' \psi^{(1)} \rangle - E^{(1)} \langle \psi^{(0)} \psi^{(1)} \rangle \qquad \text{A1.10}$$

For spin-spin coupling in molecules with singlet ground states, the calculation of $E^{(2)}$ is simplified since the first order spin-coupling energy $E^{(1)}$ is equal to zero. However, it is still necessary to obtain the first order wave function by solving Eq. A1.8(b). In general, the solution of this equation is not easy, although in some cases it can be solved analytically.

The perturbed wave functions are usually expressed in terms of an expansion of $\psi^{(1)}$ in terms of zero order excited state wave functions:

$$\psi^{(1)} = \sum_{n \neq 0} \frac{\langle \psi_n^{(0)} \mathcal{H}' \psi_0^{(0)} \rangle \psi_n^{(0)}}{E_0^{(0)} - E_n^{(0)}} \qquad \text{A1.11}$$

so that $E^{(2)}$ is given by:

$$E^{(2)} = -\sum_{n \neq 0} \frac{\langle \psi_0^{(0)} \mathcal{H}' \psi_n^{(0)} \rangle \langle \psi_n^{(0)} \mathcal{H}' \psi_0^{(0)} \rangle}{E_n^{(0)} - E_0^{(0)}} \qquad \text{A1.12}$$

where the summations are over all of the discrete states plus an integral over the continuum.

Perturbation wave functions may also be obtained

by a variational approximation. Consider a system represented by the following operators and wave functions:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \qquad \text{A1.13}$$

$$\psi = \psi^{(0)} + \tilde{\psi}^{(1)} \qquad \text{A1.14}$$

where $\mathcal{H}_0$, $\psi^{(0)}$ are the electronic Hamiltonian and ground state wave function, repectively

$\mathcal{H}'$ is the Hamiltonian representing the perturbation

$\tilde{\psi}^{(1)}$ is an arbitrary trial wave function

Then $$E = \langle \psi^{(0)} + \tilde{\psi}^{(1)} | \mathcal{H}_0 + \mathcal{H}' | \psi^{(0)} + \tilde{\psi}^{(1)} \rangle \qquad \text{A1.15}$$

assuming $\psi^{(0)}$, $\tilde{\psi}^{(1)}$ are normalized

Expanding the integral in A1.15 results in a collection of terms which may be characterized by their order in analogy to perturbation theory:

$$E^{(0)} = \langle \psi^{(0)} | \mathcal{H}_0 | \psi^{(0)} \rangle \quad \text{(0th order)} \qquad \text{A1.16(a)}$$

$$\tilde{E}^{(1)} = \langle \psi^{(0)} | \mathcal{H}' | \psi^{(0)} \rangle + \langle \tilde{\psi}^{(1)} | \mathcal{H}_0 - E^{(0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \mathcal{H}_0 - E^{(0)} | \tilde{\psi}^{(1)} \rangle$$

(1st order) A1.16(b)

$$\tilde{E}^{(2)} = \langle \tilde{\psi}^{(1)} | \mathcal{H}' | \psi^{(0)} \rangle + \langle \psi^{(0)} | \mathcal{H}' | \tilde{\psi}^{(1)} \rangle + \langle \tilde{\psi}^{(1)} | \mathcal{H}_0 - E^{(0)} | \tilde{\psi}^{(1)} \rangle$$

(2nd order) A1.16(c)

$$\tilde{E}^{(3)} = \langle \tilde{\psi}^{(1)} | \mathcal{H}' | \tilde{\psi}^{(1)} \rangle \quad \text{(3rd order)} \quad \text{A1.16(d)}$$

For spin-spin coupling in molecules with singlet ground states and $\psi^{(0)}$ orthogonal to $\tilde{\psi}^{(1)}$, $\tilde{E}^{(1)} = 0$. The spin-coupling operator $\mathcal{H}'$ changes the symmetry of the wave functions while $\mathcal{H}_0$ preserves it.

If $\mathcal{H}_0, \mathcal{H}'$ are Hermitian, the second order energy becomes:

$$\tilde{E}^{(2)} = 2 \langle \tilde{\psi}^{(1)} | \mathcal{H}' | \psi^{(0)} \rangle + \langle \tilde{\psi}^{(1)} | \mathcal{H}_0 - E^{(0)} | \tilde{\psi}^{(1)} \rangle$$

A1.17

Hylleraas' principle states that for the ground state of a system:

$$\tilde{E}^{(2)} \geq E^{(2)} \qquad \text{A1.18}$$

where $E^{(2)}$ is the exact second order perturbation energy.

The proof is as follows[27]:

Substituting for $\tilde{\psi}^{(1)} = \psi^{(1)} + \delta\tilde{\psi}^{(1)}$ in Eq. A1.17:

$$\tilde{E}^{(2)} - E^{(2)} = 2\langle \delta\tilde{\psi}^{(1)} | [(\mathcal{H}_0 - E^{(0)})\psi^{(1)} + \mathcal{H}'\psi_0] \rangle + \langle \delta\tilde{\psi}^{(1)} | \mathcal{H}_0 - E^{(0)} | \delta\tilde{\psi}^{(1)} \rangle$$

A1.19

where $\psi^{(1)}$ is the exact first order wave function. The term in δ vanishes because of Eq. A1.8(b) and the term in δ^2 is positive because $E^{(0)}$ is the lowest eigenvalue of $\mathcal{H}_0$, so $E^{(2)} - E^{(2)}$ is positive. Notice that if $\tilde{\psi}^{(1)} = \psi^{(1)}$, then Eq. A1.17 should be equivalent to A1.10. This means that if $\tilde{\psi}^{(1)}$ is the exact first order wave function then:

$$\langle \tilde{\psi}^{(1)} | \mathcal{H}_0 | \tilde{\psi}^{(1)} \rangle = -\langle \tilde{\psi}^{(1)} | \mathcal{H}' | \psi^{(0)} \rangle$$

A1.20

Usually the first order equation A1.8(b) cannot be solved analytically. The perturbation-variation method approximates $E^{(2)}$ and $\psi^{(1)}$ by inserting a trial function $\tilde{\psi}^{(1)}$ in Eq. 1.17 and making $\tilde{E}^{(2)}$ stationary with respect to the variational parameters present in $\tilde{\psi}^{(1)}$. In cases where $\psi^{(0)}$ is not known exactly, Eq. 1.17 may still be used to approximate $\psi^{(1)}$ by making $\tilde{E}^{(2)}$ stationary, but $\tilde{E}^{(2)}$ is no longer a correct variational approximation to $E^{(2)}$.

Spin-spin coupling constants are sometimes calculated using double perturbation theory. Recasting

Eq. A1.13 and A1.14 as a double perturbation one has:

$$\mathcal{H}' = \mu \mathcal{H}_{10} + \nu \mathcal{H}_{01} \qquad \text{A1.21}$$

$$\psi^{(1)} = \mu \psi_{10} + \nu \psi_{01} \qquad \text{A1.22}$$

Equation A1.16(c) can be expanded and divided into self-terms and cross-terms:

$$\tilde{E}^{(2)} = \mu^2 \tilde{E}_{20} + \nu^2 \tilde{E}_{02} + \mu\nu \tilde{E}_{11} \qquad \text{A1.23}$$

where

$$\mu^2 \tilde{E}_{20} = 2\langle \psi_{00} | \mu \mathcal{H}_{10} | \mu \psi_{10} \rangle + \langle \mu \psi_{10} | \mathcal{H}_0 - E_{00} | \mu \psi_{10} \rangle \qquad \text{A1.24}$$

$$\nu^2 \tilde{E}_{02} = 2\langle \psi_{00} | \nu \mathcal{H}_{01} | \nu \psi_{01} \rangle + \langle \nu \psi_{01} | \mathcal{H}_0 - E_{00} | \nu \psi_{01} \rangle \qquad \text{A1.25}$$

$$\mu\nu \tilde{E}_{11} = 2\langle \psi_{00} | \mu \mathcal{H}_{10} | \nu \psi_{01} \rangle + 2\langle \psi_{00} | \nu \mathcal{H}_{01} | \mu \psi_{10} \rangle + 2\langle \mu \psi_{10} | \mathcal{H}_0 - E_{00} | \nu \psi_{01} \rangle \qquad \text{A1.26}$$

Equation A1.26 may be further simplified by using Dalgarno's interchange theorem,[27,58,59] which states that any integral involving $\mathcal{H}_{01}\psi_{10}$ may be interchanged for others involving $\mathcal{H}_{10}\psi_{01}$. Hence the equation becomes:

$$\mu\nu\tilde{E}_{11} = 4\langle\psi_{00}|\mu\mathcal{H}_{10}|\nu\psi_{01}\rangle + 2\langle\mu\psi_{10}|\mathcal{H}_0 - E_{00}|\nu\psi_{01}\rangle \qquad \text{A1.26(a)}$$

Das and Bersohn[35] showed that the Hylleraas Variational principle also applies to the second order energy in Eq. A1.23. In spin-spin coupling calculations, ψ_{00} is rarely, if ever, exact. However, the variational principle would fail only if the total wave function (Ψ) or the difference between the exact first order perturbation function and the trial wave function ($\delta\tilde{\Psi}^{(1)}$) were a better approximation to the lowest wave function than ψ_{00}.

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