(i)

DETERMINATION OF THE DONOR PAIR EXCHANGE ENERGY
IN PHOSPHORUS-DOPED SILICON

by

PIETER RUTTER CULLIS

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department
of
Physics

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1970

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study.

I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia
Vancouver 8, Canada

Date April 17, 1970

(ii)

ABSTRACT

The e.p.r. spectrum for relatively dilute samples of phosphorus-doped silicon ($<5 \times 10^{16}$ donors/cm³) has been calculated in detail for an assumed random distribution of impurities. The system of donor electron spins is treated as a collection of nearest neighbor donor pairs. An expression is derived for the donor pair exchange energy using Kohn-Luttinger wavefunctions and a general exchange energy expression. The resultant relationship contains an adjustable parameter a^* , the "effective Bohr radius", which is determined from a comparison of the calculated spectrum and the experimental results obtained for the ratio, C , of the "central pair" and "hyperfine" line intensities. The resulting expression $J(\underline{R})$, where J represents the exchange energy and $\underline{R}$ the separation vector connecting the two pair donors, exhibits an oscillatory spatial dependence due to interference from portions of the wavefunction arising from different conduction band valleys.

TABLE OF CONTENTS

	PAGE
ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	v
LIST OF TABLES	vi
ACKNOWLEDGEMENTS	vii
CHAPTER	
I. INTRODUCTION	1
II. THEORY	3
A. Electron Spin Resonance	3
B. The Wavefunctions of the Impurity States	4
C. The Nearest Donor Approximation	5
D. The Exchange Interaction	6
E. The Donor Pair System	7
III. CALCULATION OF THE SPECTRUM	9
A. Introduction	9
B. Matrix Element Calculations	10
C. Calculation of the Population Difference Between Transition Levels	18
D. The Theoretical Spectrum	21
IV. EXPERIMENTAL METHODS AND RESULTS	22
A. Apparatus and Operating Conditions	22
B. Experimental Results	25
C. Possible Error	29
V. DISCUSSION OF RESULTS	30
BIBLIOGRAPHY	31
APPENDIX	
A. POPULATION DIFFERENCES BETWEEN TRANSITION LEVELS	32
B. CALCULATION OF EXCHANGE	34

APPENDIX

PAGE

C. THE DISTRIBUTION OF NEAREST EXCHANGE COUPLED PAIRS . .	38
a. Calculation of the Number of Lattice Sites in Shells of Unit Thickness Centred on the Origin	38
b. Determination of the Nearest Neighbour Distribution	41
D. CALCULATION OF THE THEORETICAL SPECTRUM	47

LIST OF FIGURES

FIGURE	PAGE
1. Energy Levels of a Spin $\frac{1}{2}$ System	3
2. Energy vs. k Relation in $[1,0,0]$ Direction	4
3. Spin System of the Pair	7
4. Spectrum of the Pair System	8
5. Energy Level Diagram for a Phosphorus Donor Pair. The Eigenstates are Labelled Numerically From 1 to 16 Along With the Usual Strongly Coupled Pair States to Which Each Reduces in the Limit $J \gg A$	17
6. Spectral Contributions of Allowed Transitions	12
7. Comparison of Discrete and Continuous $N(J)$ ($a^* = 16.5 \text{\AA}$)	20
8. Introduction of the Gaussian Shape Function	21
9. Block Diagram of Experimental Apparatus	24
10. Mode Shape and Sample Cavity Resonance	22
11. Experimental ESR Derivative Trace for $N_d = 3.7 \times 10^{16} / \text{cm}^3$	26
12. A Plot of Experimental Points and Theoretically Calculated Values of the Ratio $C(\%)$ of the Central Pair Line Intensity to the Average Intensity of the Hyperfine Lines. The Line Represents the Calculated Ratio for an Effective Bohr Radius $a^* = 17.3 \text{\AA}$	27
13. A Plot of the Normalized Distribution of Pair J Values $N(J)/N_0/2$ as a Function of the Exchange Energy J for a 4×10^{16} Donors / cm^3 Sample (Solid Curve) and a 6×10^{16} Donors / cm^3 Sample (Dashed Curve)	28
14. Simple Face Centred Cubic Lattice Structure	38
15. Simplified Energy Level Diagram of the Donor Pair	32

LIST OF TABLES

TABLE	PAGE
I. Matrix Representation of the Hamiltonian of the Donor Pair System	13
II. Eigenfunctions of the Donor Pair	14
III. A Comparison of (i) the Computer Projected Donor Pair Eigenvalues When the Off-diagonal Hyperfine Elements are not Neglected to (ii) the Functional Derivation Where These Off-diagonal Elements are Neglected	15
IV. Donor Pair Transitions Having Non-zero Transition Probability. The Relative Transition Probabilities and the Transition Energies, Δ , are Given and $\gamma_e = gBH_0$	16
V. Boltzmann Population Differences Between Transition Levels	33
VI. Number of Lattice Sites Having the Same Absolute Value for Projections on the x, y, z Axes in a Crystal with Interlocking F.C.C. Structure	40

ACKNOWLEDGEMENTS

I would like to thank Dr. John R. Marko for his suggestion of the thesis topic and subsequent encouragement through all phases of the problem.

Thanks also go to Dr. R. Barrie, who was a critical sounding-board for many aspects of this thesis.

I would like to express gratitude to the National Research Council for their award of a Post Graduate Studentship for the duration of this work.

The research for this thesis was supported by the National Research Council, Grant Number 67-4624.

CHAPTER I

INTRODUCTION

The electron spin resonance (E.S.R.) spectrum of phosphorus doped silicon (P-Si) in the concentration range $10^{15} < N < 10^{18}$ impurities /cm³ demonstrates a "weak centre peak" that lies midway between the hyperfine lines of the isolated donors. Slichter¹ attributed this peak to coupled pairs of neighbouring impurities that act as a unit with a total spin of 1. In samples with $N_d < 5 \times 10^{16}$ /cm³ ancillary lines adjacent to the centre peak have similarly been explained in terms of clusters of three or more donor atoms.

The degree to which two interacting spins may be considered to act as a pair is given by the exchange energy "J" between them. Slichter's calculation included only those pairs for which $J \sim A$, where A is the hyperfine interaction. It is the purpose of this work to determine the functional dependence of J on "r", the interdonor separation, for all values of r. This functional dependence is constructed so as to contain a single adjustable parameter a^* , the "effective Bohr radius" of the impurity electron, which is subsequently fitted to experimental results.

Motivation for the determination of J arises partly from the "spin diffusion" mechanism that can transport energy from one part of a spectral line to another², presumably via a flip-flop of neighbouring spins. It has been proposed that the bulk of electronic spins relax through such a diffusion of spin and energy to other spin centres with very short spin lattice relaxation times, " T_1 ". One of these fast relaxing centres is suspected to be³ the previously mentioned highly coupled pair, with $T_1 \propto J^{-2}$. A functional knowledge of J is therefore essential before detailed studies of the spin diffusion relaxation mechanism can be initiated.

Attention has also been given to a broad background line that

has been observed beneath the isolated donor spectrum of P-Si and which extends well outside this spectrum. This line is thought to arise from exchange coupled pairs for which $J \sim A$. It is shown that at least part of this line is due to such pairs.

CHAPTER II

THEORY

A. Electron Spin Resonance

The basic energy levels of the unpaired electrons of a paramagnetic sample in a magnetic field $\underline{H} = H_0 \hat{k}$ are given in Figure 1.

m_s = the electronic spin quantum number
 $h\gamma_{12}$ = energy difference between states
 N^+ = number of electrons in upper state
 N^- = number of electrons in lower state

Figure 1. Energy levels of a spin $\frac{1}{2}$ system.

If this system is subjected to a microwave field at frequency γ_{12} , the resulting equilibrium absorption of energy (ESR) can be written (assuming no saturation)⁴ as:

$$A = n_{ss} |C_{-\frac{1}{2}, \frac{1}{2}}|^2 h \gamma_{12} g(\gamma_{12}) \quad (1-1)$$

where $C_{-\frac{1}{2}, \frac{1}{2}}$ is the matrix element connecting the states, $g(\gamma_{12})$ is a "shape function" due to the finite width of the energy levels, and n_{ss} is the steady state excess number of electrons in the ground state. Assuming Boltzmann population statistics (see Appendix I) we obtain:

$$n_{ss} = N \sinh \left[\frac{h \gamma_{12}}{2kT} \right] \quad (1-2)$$

where N is the total number of spins, k is Boltzmann's constant, and

T is the absolute temperature in $^{\circ}\text{K}$. Examination of equation 1-2 reveals that the greatest population differences and hence the largest ESR signals are obtained at high magnetic fields and low temperatures.

B. The Wavefunctions of the Impurity States

Silicon has six conduction band minima in "k" space that lie along each of the directions $[1,0,0]$, $[-1,0,0]$, $[0,1,0]$, $\dots$, $[0,0,-1]$ as shown in Figure 2.

Figure 2. Energy vs k relationship in the $[1,0,0]$ direction.

The wavefunctions of the impurity states can be represented⁵ by the following linear combination of the wavefunctions at each of these conduction band minima:

$$\Psi(\mathbf{r}) = F(\mathbf{r}) \sum_{n=1}^6 \alpha_n e^{i\mathbf{k}_0^{(n)} \cdot \mathbf{r}} u_{\mathbf{k}_0^{(n)}}(\mathbf{r}) \quad (1-3)$$

where α_n represents the contribution of each minimum to the total wavefunction, and $U_{\mathbf{k}_0^{(n)}}(\mathbf{r})$ is a periodic function of $\mathbf{r}$ corresponding to the n^{th} minimum. $F(\mathbf{r})$ is an envelope function satisfying a hydrogen-like Schroedinger equation:

$$\left[-\frac{\hbar^2}{2m_l} \frac{\nabla^2}{\nabla^2} - \frac{\hbar^2}{2m_t} \left(\frac{\nabla^2}{\nabla^2} + \frac{\nabla^2}{\nabla^2} \right) \right] F(\mathbf{r}) - \frac{e^2}{kr} F(\mathbf{r}) = E F(\mathbf{r}) \quad (1-4)$$

where m_l is the longitudinal effective mass, m_t is the transverse

effective mass, e is the electronic charge and K is the macroscopic dielectric constant. Equation 1-4 is non-separable, but a good variational solution to it⁶ is given by:

$$F(r) = \frac{1}{\sqrt{\pi a^2 b}} e^{-\sqrt{\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2}}} \quad (1-5)$$

where a and b are, respectively, the transverse and longitudinal "effective Bohr radii".

As previously mentioned, this work will employ a single effective Bohr radius that enables equation 1-5 to be rewritten as:

$$F(r) = \frac{1}{\sqrt{\pi a^{*3}}} e^{-\frac{r}{a^*}} \quad (1-6)$$

where a^* is presumably some suitable average of a and b .

Kohn⁵ finds, from considerations of symmetry and the experimentally observed ground state hyperfine splitting that $n = 1/\sqrt{6}$ for all n . Therefore we can write equation 1-3 for the ground state as:

$$\Psi(r) = \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{\pi a^{*3}}} \cdot e^{-\frac{r}{a^*}} \sum_{n=1}^6 e^{i \underline{k}_0^{(n)} \cdot \underline{r}} u_{\underline{k}_0^{(n)}}(r) \quad (1-7)$$

The interference term $e^{i \underline{k}_0^{(n)} \cdot \underline{r}}$ in equation 1-7 will be retained explicitly in our further calculations.

C. The Nearest Donor Approximation

This study assumes a random distribution of the phosphorus impurities in the host lattice. This assumption has previously been shown to be reasonably justified in the concentration range of interest.⁷ Further, we assume that the exchange interaction J between donor electrons is non-negligible for nearest neighbours only. Obviously, this approximation becomes inaccurate when some impurity site "A" is the same distance from neighbouring sites "B" and "C", but it is found that, for our concentration range, non-negligible probabilities of such clusters arise only when A, B and

C are so widely separated as to act like isolated donors. This approximation is also justified by the absence of lines due to such clusters in our spectra.

D. The Exchange Interaction

The nearest neighbour exchange interaction may be written as⁸:

$$V_{ex} = J \underline{S}_1 \cdot \underline{S}_2 \quad (1-8)$$

where $\underline{S}_1$, $\underline{S}_2$ are the spins of the two electrons concerned, and:

$$J = - \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^2}{r_{12}} \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \psi_1(\mathbf{r}_2) \psi_2(\mathbf{r}_1) \\ - 2 \iint \psi_1^*(\mathbf{r}_1) \psi_2(\mathbf{r}_1) d\mathbf{r}_1 \cdot \psi_1^*(\mathbf{r}_2) \left(-\frac{e^2}{r_{12}} \right) \psi_2(\mathbf{r}_2) \quad (1-9)$$

$$\equiv - \bar{J}_{12}^0 - 2 S_{12} L_{12} \quad (1-10)$$

where ψ_1 , ψ_2 are the wavefunctions of electrons 1 and 2, and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

We can now calculate the exchange energy J as a function of interdonor separation $\underline{r}$ by substituting the impurity wavefunctions of equation 1-7 into equation 1-9. This is done in Appendix II, where we obtain:

$$J(r) = \frac{1}{9} \frac{e^2}{\kappa_0 a^*} \left(\sum_n \cos(\mathbf{k}_n^{(n)} \cdot \underline{r}) \right)^2 e^{-2D} \left\{ 2(1+D) \left(1+D + \frac{D^2}{3} \right) \right. \\ \left. - \frac{1}{5} \left[- \left(-\frac{25}{8} + \frac{23D}{4} + 3D^2 + \frac{D^3}{3} \right) + \frac{6}{D} \left[\left(1+D + \frac{D^2}{3} \right)^2 (8+14D) \right] \right] \right\} \quad (1-11)$$

The $\left(\sum_n \cos \mathbf{k}_n^{(n)} \cdot \underline{r} \right)^2$ factor represents an interference effect due to contributions from various conduction band minima.

E. The Donor Pair System

It is instructive to first calculate the donor pair spectrum in the two limiting cases of large ($J \gg A$) and small ($J \ll A$) exchange energy. The spin system is given in Figure 3.

Figure 3. Spin system of the pair.

The Hamiltonian for this system can be written as:

$$\mathcal{H} = g\beta H [\underline{S}_{1z} + \underline{S}_{2z}] + A[\underline{I}_1 \cdot \underline{S}_1 + \underline{I}_2 \cdot \underline{S}_2] + J \underline{S}_1 \cdot \underline{S}_2 \quad (1-12)$$

where g is the electronic g factor and β is the Bohr magneton. The much smaller nuclear Zeeman and nuclear spin-spin interactions are neglected. In the limit $J \ll A$, the resulting spectra is obviously that of the isolated donor, which gives two hyperfine peaks at $E = g\beta H_0 \pm A/2$. The more interesting limit when $J \gg A$ shall now be considered in detail. For this situation $\underline{S} = \underline{S}_1 + \underline{S}_2$ is essentially a good quantum number. Neglecting the off-diagonal components of the hyperfine interaction, which is justified for ^{almost} all values of J (c.f. Chapter II, Section B), equation 1-12 becomes:

$$\mathcal{H} = g\beta H S_z + A S_z (\underline{I}_{1z} + \underline{I}_{2z}) + \frac{J}{2} (S^2 - \frac{1}{2}) \quad (1-13)$$

with eigenvalues:

$$E_T^{0,\pm 1} = g\beta H M + \frac{1}{2} A M (m_1 + m_2) + \frac{J}{4} \quad (1-14)$$

and

$$E_S = -\frac{3}{4} J \quad (1-15)$$

where E_T , E_S are the triplet and singlet energies (using the usual notation for the ground state of the hydrogen molecule). M is the total electronic spin projection quantum number, and m_1 , m_2 are the individual nuclear spin projection numbers.

The introduction of a microwave field adds a perturbation to the Hamiltonian $\mathcal{H}$ of the form:

$$\mathcal{H}_{r.f.} = \frac{g\beta H_1}{2} (S^+ + S^-) \sin(\omega t) \quad (1-16)$$

where S^+ is the electron spin raising operator, S^- is the electron spin lowering operator, and $\omega/2\pi$ is the frequency of transition. Clearly, this perturbation induces transitions such that $\Delta M = \pm 1$, $\Delta(m_1 + m_2) = 0$.

The transition $\Delta S = 1$ is not allowed. This is due to the fact that the spin wavefunctions of the triplet state are symmetric under interchange of electrons, whereas those of the ground state are antisymmetric under the same operation. Thus $\mathcal{H}_{r.f.}$, symmetric under this interchange, cannot connect the singlet to the triplet because of parity considerations. Note that when $J \sim A$, however, S is no longer a good quantum number and we observe² such "forbidden" transitions from the "singlet" to the "triplet" states.

From the selection rules given above, the ESR spectrum will have the form of Figure 4.

Figure 4. Spectrum of the pair system.

Note that the spectra due to the isolated donors will effectively mask the donor pair peaks at $E = g\beta H_0 \pm A/2$.

CHAPTER III

CALCULATION OF THE SPECTRUM

A. Introduction

The spectrum of P-Si is inhomogeneously broadened due to hyperfine interactions with Si^{29} nuclei (4% natural abundance). The following calculation will assume the existence of the "spin packets" proposed by Portis⁹. Each such spin packet constitutes a homogeneously broadened line corresponding to a particular effective local field, and has little interaction with those packets corresponding to different local fields. This is a questionable assumption and should be considered in more detail in future studies. For each of these packets the susceptibility $\chi = \chi' + i\chi''$ is given by⁹:

$$\chi'(H) = \frac{1}{2} \chi_0 \gamma^2 H_0 T_2^2 \frac{(H_0 - H)}{1 + T_2^2 \gamma^2 (H_0 - H)^2 + \gamma^2 H_1^2 T_1 T_2} \quad (2-1)$$

$$\chi''(H) = \frac{1}{2} \chi_0 \gamma H_0 T_2 \frac{1}{1 + T_2^2 \gamma^2 (H_0 - H)^2 + \gamma^2 H_1^2 T_1 T_2} \quad (2-2)$$

where χ_0 is the static magnetic susceptibility, γ is the free electron gyromagnetic ratio, H_1 is the microwave magnetic field intensity, T_1 and T_2 are the spin-lattice and spin-spin relaxation times respectively, and H_0 is the central resonant field of the spin packet.

Experimentally, we observe $d\chi'/dH$. Thus, realizing that for our low concentration samples ($< 4 \times 10^{16}/\text{cm}^3$) $\gamma^2 H_1^2 T_1 T_2 \gg T_2^2 \gamma^2 (H - H_0)^2$ when $H \approx H_0$, we obtain from equation 2-1 that:

$$\left(\frac{d\chi'(H)}{dH} \right)_{H \approx H_0} \approx \frac{\frac{1}{2} \chi_0 \gamma^2 H_0 T_2^2}{1 + \gamma^2 H_1^2 T_1 T_2} \quad (2-3)$$

and thus from equation 2-2,

$$\left(\frac{d\chi''(H)}{dH} \right)_{H \approx H_0} \approx \gamma T_2 \chi''(H_0) \quad (2-4)$$

Then, given that the rate of power absorbed by the sample is⁹:

$$A = 2 \gamma H_0 \chi''(H_0) \quad (2-5)$$

we obtain from equations 1-1 and 2-4 that:

$$\left(\frac{d\chi'(H)}{dH} \right)_{H=H_0} \propto n_{ss} \left| C_{-\frac{1}{2}, \frac{1}{2}} \right|^2 g(H-H_0) \quad (2-6)$$

where we assume a shape function $g(H-H_0)$ for the homogeneously broadened line of each spin packet to be of a Gaussian form. A theoretical calculation of a scale model of the spectrum therefore involves determining each of the terms on the right hand side of equation 2-6 over each interval of H corresponding to a spin packet width.

B. Matrix Element Calculations.

The calculation of the matrix elements of the allowed transitions necessitates a general calculation of the eigenvalues and eigenfunctions of the donor pair system over the whole range of J . Following the individual spin notation introduced in Figure 3, we can write the general form of the eigenfunctions as :

$$\Psi^{(n)} = \sum_{i,j,k,l=1}^2 C_{ijkl}^{(n)} |M_i M_j m_k m_l\rangle \quad (2-7)$$

where M_1, M_2 are the "z" components of the electronic spins $\underline{S}_1$ and $\underline{S}_2$, m_1 and m_2 are the "z" components of the nuclear spins $\underline{I}_1$ and $\underline{I}_2$, and the $C_{ijkl}^{(n)}$'s are normalized constants giving the contribution to the eigenfunction from each of the basis states.

There are 16 basic wavefunctions $\Psi_{ijkl} = |M_i M_j m_k m_l\rangle$ and correspondingly 16 $C_{ijkl}^{(n)}$'s for a given $\Psi^{(n)}$. The matrix representation of the Hamiltonian of the donor pair spin system (equation 1-12) in this basis is given in Table I. This matrix was diagonalized via computer and the corresponding eigenvalues and eigenfunctions determined for particular values of J . The eigenfunctions compiled in Table II have a particular form which guarantees that they be invariant under the

simultaneous interchange of both electron and nuclear spins (this operation commutes with the Hamiltonian given in equation 1-12.).

As this calculation of the eigenvectors and eigenvalues of for each value of J was tedious and costly in computer time, we determined their functional form by means of a hybrid method. Labelling the basis vectors χ_m by unprimed m, n 's, and the eigenvectors (in the diagonal representation) by m', n', we write

$$\begin{aligned} |m'\rangle &= \sum_m |m\rangle \langle m|m'\rangle \\ &= \sum_m |m\rangle C_{mm'} \end{aligned} \quad (2-8)$$

where the $C_{mm'}$ have already been calculated via computer for certain J's.

Then:

$$\mathcal{H} |m'\rangle = E_{m'} |m'\rangle = \sum_m \mathcal{H} |m\rangle C_{mm'} \quad (2-9)$$

or:

$$E_{m'} \langle n|m'\rangle = \sum_m \langle n|\mathcal{H}|m\rangle C_{mm'} \quad (2-10)$$

which we express more concisely as:

$$E_{m'} C_{nm'} = \sum_m H_{nm} C_{mm'} \quad (2-11)$$

In accord with equation 2-11 the n^{th} row of H_{nm} was multiplied by the column vector $|m'\rangle$ and the equation was solved for the corresponding $E_{m'}$. This calculation was facilitated by neglecting the off-diagonal elements of the hyperfine interaction. A check on this approximation was made by comparing the eigenvalues projected by computer (in which the off-diagonal elements were not neglected) and the calculated $E_{m'}$ in the region $J \sim A$, with gratifying results (See Table III). The functional $E_{m'}$'s are given in Table II and the energy level structure in Figure 5, where S, T_0 , and $T_{\pm 1}$ refer to electronic pair spin states, and $s, t_0, t_{\pm 1}$ refer to similar

nuclear pair spin states, in the $J \gg A$ limit.

The non-zero values of the matrix elements connecting the various states under the influence of the microwave radiation are now easily calculated and are given in Table IV, together with the corresponding transition energy " Δ ". Examination of Δ reveals the different regions of the spectrum to which each transition contributes. This is illustrated in Figure 6.

Figure 6. Spectral contributions of allowed transitions.

The broad background line is shown to be at least partly due to donor pairs for which $J \sim A$.

TABLE I

Matrix Representation of the Hamiltonian of the Donor Pair System

$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix} \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \end{pmatrix}$
$\delta H_0 + \frac{J}{4} A$																
	$\delta H_0 + \frac{J}{4}$			$\frac{A}{2}$												
		$\delta H_0 + \frac{J}{4}$						$\frac{A}{2}$								
			$\delta H_0 + \frac{J}{4} A$			$\frac{A}{2}$		$\frac{A}{2}$								
	$\frac{A}{2}$			$-\frac{J}{4}$				$\frac{J}{2}$								
					$\frac{J}{4} + \frac{A}{2}$			$\frac{J}{2}$								
			$\frac{A}{2}$			$-\frac{J}{4} - \frac{A}{2}$			$\frac{J}{2}$		$\frac{A}{2}$					
							$-\frac{J}{4}$			$\frac{J}{2}$		$\frac{A}{2}$				
		$\frac{A}{2}$		$\frac{J}{2}$				$-\frac{J}{4}$								
			$\frac{A}{2}$		$\frac{J}{2}$				$-\frac{J}{4} - \frac{A}{2}$		$\frac{A}{2}$					
						$\frac{J}{2}$				$-\frac{J}{4} + \frac{A}{2}$						
							$\frac{J}{2}$				$-\frac{J}{4}$			$\frac{A}{2}$		
					$\frac{A}{2}$			$\frac{A}{2}$				$-\delta H_0 + \frac{J}{4} A$				
						$\frac{A}{2}$							$-\delta H_0 + \frac{J}{4}$			
										$\frac{A}{2}$				$-\delta H_0 + \frac{J}{4}$		
															$-\delta H_0 + \frac{J}{4} A$	

TABLE II

Eigenfunctions of the Donor Pair

State	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline \end{array}$	Energy
1	1																$8H_0 + \frac{J}{4} + \frac{A}{2}$
2		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$														$8H_0 + \frac{J}{4}$
3		$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$														$8H_0 + \frac{J}{4}$
4				1													$8H_0 + \frac{J}{4} - \frac{A}{2}$
5					$\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$								$\frac{J}{4}$
6					$-\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$								$-\frac{3J}{4}$
7						a_1	a_2			a_2	a_1						$-\frac{J}{4} + \frac{1}{2}\sqrt{J^2 + A^2}$
8						a_1	$-a_2$			a_2	$-a_1$						$-\frac{J}{4} + \frac{1}{2}\sqrt{J^2 + A^2}$
9								$\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$					$\frac{J}{4}$
10								$-\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$					$-\frac{3J}{4}$
11						a_2	a_1			$-a_1$	$-a_2$						$-\frac{1}{2}\sqrt{J^2 + A^2} + \frac{A}{2}$
12						a_2	$-a_1$			$-a_1$	a_2						$-\frac{1}{2}\sqrt{J^2 + A^2} + \frac{A}{2}$
13														1			$-8H_0 + \frac{J}{4} - \frac{A}{2}$
14													$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$			$-8H_0 + \frac{J}{4}$
15													$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$			$-8H_0 + \frac{J}{4}$
16																1	$-8H_0 + \frac{J}{4} + \frac{A}{2}$

TABLE III

A Comparison of (i) the Computer Projected Donor Pair Eigenvalues When the Off-diagonal Hyperfine Elements are not Neglected to (ii) the Functional Derivation Where These Off-diagonal Elements are Neglected.

State	J = 25 MHz		J = 400 MHz	
	(i)	(ii)	(i)	(ii)
1	10065.25	10065.25	10159.	10159.
2	10007.59	10006.25	10101.	10100.
3	10005.59	10006.25	10099.	10100.
4	9947.9	9947.25	10041.	10041.
5	6.59	6.25	99.7	100.
6	-18.39	-18.75	-299.6	-300.
7	54.06	54.06	108.5	108.5
8	54.06	54.06	108.5	108.5
9	5.9	6.25	100.3	100.
10	-22.46	-18.75	-300.3	-300.3
11	-66.56	-66.56	-308.5	-308.5
12	-66.56	-66.56	-308.5	-308.5
13	-10053.5	-10052.75	-9959.7	-9959.
14	-99941.1	-9993.75	-9900.	-9900.
15	-9994.1	-9993.75	-9900.	-9900.
16	-9934.75	-9934.75	-9841.	-9841.

TABLE IV

Donor Pair Transitions Having Non-zero Transition Probability. The Relative Transition Probabilities and the Transition Energies, Δ , are Given and $\mathcal{V}_e = g\beta H_0$.

Transition	Relative Transition Probability	Transition Energy (Δ)
a: (16) $\leftrightarrow$ (9)	1	$\mathcal{V}_e - \frac{A}{2}$
b: (13) $\leftrightarrow$ (5)	1	$\mathcal{V}_e + \frac{A}{2}$
c: (9) $\leftrightarrow$ (4)	1	$\mathcal{V}_e - \frac{A}{2}$
d: (5) $\leftrightarrow$ (1)	1	$\mathcal{V}_e + \frac{A}{2}$
e: (15) $\leftrightarrow$ (8)	$\frac{1}{2}(1 + J(J^2 + A^2)^{-\frac{1}{2}})$	$\mathcal{V}_e + \frac{1}{2}(J^2 + A^2)^{\frac{1}{2}} - \frac{J}{2}$
f: (14) $\leftrightarrow$ (7)	"	"
g: (8) $\leftrightarrow$ (3)	"	$\mathcal{V}_e - \frac{1}{2}(J^2 + A^2)^{\frac{1}{2}} + \frac{J}{2}$
h: (7) $\leftrightarrow$ (2)	"	"
i: (15) $\leftrightarrow$ (11)	$\frac{1}{2}(1 - J(J^2 + A^2)^{-\frac{1}{2}})$	"
j: (14) $\leftrightarrow$ (12)	"	"
k: (12) $\leftrightarrow$ (2)	"	$\mathcal{V}_e + \frac{1}{2}(J^2 + A^2)^{\frac{1}{2}} + \frac{J}{2}$
l: (11) $\leftrightarrow$ (3)	"	"

FIGURE 5

STATE NO.		STATE	ENERGY ($\gamma_e = g\beta H$)
1	—————	$ T_i, t_i\rangle$	$\gamma_e + \frac{J}{4} + \frac{A}{2}$
2&3	—————	$ T_i, t_o\rangle, T, s\rangle$	$\gamma_e + \frac{J}{4}$
4	—————	$ T_i, t_{-i}\rangle$	$\gamma_e + \frac{J}{4} - \frac{A}{2}$
5&9	—————	$ T_o, t_i\rangle, T_o, t_{-i}\rangle$	$\frac{J}{4}$
7&8	—————	$ T_o, t_o\rangle, T_o, s\rangle$	$-\frac{J}{4} + \frac{1}{2} \sqrt{J^2 + A^2}$
16	—————	$ T_{-i}, t_{-i}\rangle$	$-\gamma_e + \frac{J}{4} + \frac{A}{2}$
14&15	—————	$ T_{-i}, t_o\rangle, T, s\rangle$	$-\gamma_e + \frac{J}{4}$
13	—————	$ T_{-i}, t_i\rangle$	$-\gamma_e + \frac{J}{4} - \frac{A}{2}$
6&10	—————	$ S, t_i\rangle, S, t_{-i}\rangle$	$-\frac{3J}{4}$
11&12	—————	$ S, t_o\rangle, S, s\rangle$	$-\frac{J}{4} - \frac{1}{2} \sqrt{J^2 + A^2}$

Energy Level Diagram for a Phosphorus Donor Pair. The Eigenstates are Labelled Numerically From 1 to 16 Along With the Usual Strongly Coupled Pair States to Which Each Reduces in the Limit $J \rightarrow A$.

C. Calculation of the Population Difference Between Transition Levels

The population difference between the transition levels is given by n_{ss} as defined by equation 1-2. The determination of n_{ss} thus entails a knowledge of the relative number of pairs that contribute to a given spin packet, and also of the normalized distribution of spins in the corresponding upper and lower states at equilibrium. Appendix A deals with the latter calculation. As the transition energies Δ can be written in terms of J (Table IV), we shall calculate $N(J)$, (the normalized distribution of nearest donor pairs having J values in a certain range) in order to find the relative number of pairs contributing to a given spin packet.

The nearest neighbour distribution function for a random distribution of impurities is given by Chandresklar¹⁰ as:

$$W(r) dr = e^{-\frac{4\pi N_d r^3}{3}} \frac{4\pi N_d r^2 dr}{3} \quad (2-12)$$

where N_d is the concentration of impurities and $W(r)dr$ is the probability that the nearest neighbour to a given impurity lies in the spherical shell between r and $r + dr$. Noting that the factor $4\pi N_d r^3/3$ in equation 2-12 expresses the number of impurity sites inside a radius r , we write:

$$\frac{4\pi N_d r^3}{3} = \frac{N_d}{N_{SI}} \cdot n(r) \quad (2-13)$$

where $n(r)$ is the total number of lattice sites inside " r ", and N_{SI} is the concentration of lattice sites. Similarly:

$$4\pi N_d r^2 dr = \frac{N_d}{N_{SI}} \cdot n(r, r+dr) \quad (2-14)$$

and therefore equation 2-12 can be rewritten as:

$$W(r) dr = \frac{N_d}{N_{SI}} n(r, r+dr) e^{-\frac{N_d}{N_{SI}} n(r)} \quad (2-15)$$

The probability that any particular lattice site in the shell is

a nearest donor impurity site is then given by:

$$P(r) = \frac{N_d}{N_{SI}} e^{-\frac{N_d}{N_{SI}} \cdot r(r)} \quad (2-16)$$

For particular values of N_d and a^* , the determination of $N(J)$ entails calculating J for each lattice site in a particular shell. Then, the probability that this lattice site is a nearest donor impurity site (as given by equation 2-16) is associated with this value of J . This analysis can then be performed over all possible shells, and the probabilities $P(r)$ (whose J 's fit into certain intervals) added in a corresponding array. Thus, for a particular concentration and effective Bohr radius, a discrete $N(J)$ is determined. The computer analysis necessary to this computation is contained in Appendix C.

In order to make further calculation easier, a continuous $N(J)$ was calculated by taking an appropriate average of the interference term in equation 1-11 (c.f. Appendix C). A comparison of the discrete and continuous distributions for $N_d = 4 \times 10^{16}/\text{cm}^3$ and $a^* = 16.5\text{\AA}$ is given in Figure 7. (The rapid fall-off of the discrete curve in the region $\log J < -1$ is simply due to the fact that not all the pairs in this region were considered, due to limitations of computer time.)

The problem of determining the relative number of spins that contribute to a certain spin packet is now reduced to an integration of $N(J)$ over the width of the packet expressed in terms of J . This is combined with the normalized Boltzmann population differences between the levels (Appendix A) to give ρ_{ss} of equation 2-6.

FIGURE 7

Comparison of Discrete and Continuous $N(J)$ ($a^*=16.5\text{\AA}$)

D. The Theoretical Spectrum

The final step in the calculation consists first of integrating the absorption A over one spin packet. We obtain $N_{\bar{J}_1}^{\bar{J}_2}$ where:

$$N_{\bar{J}_1}^{\bar{J}_2} = \int_{J_1}^{\bar{J}_2} N(J) \cdot f_B(J, \Delta, T) \cdot M_{ij}^2(J) dJ \quad (2-17)$$

where $E(J_1) - E(J_2)$ is the spin packet width, $f_B(J, \Delta, T)$ is the normalized Boltzmann population difference between the i and j levels, $M_{ij}(J)$ is the matrix element connecting the i and j states, and T is the temperature in $^{\circ}\text{K}$. With reference to Figure 8, the Gaussian shape function is then introduced.

Figure 8. Introduction of the Gaussian shape function.

The total absorption $N_{\bar{J}_1}^{\bar{J}_2}$ is taken to be the area under the Gaussian shape function, with half width equal to the spin packet width ($\sim 8\text{MHz}$). The convolution of all these contributing Gaussians is then calculated and the resulting scaled spectrum is obtained. Appendix D presents the computer program that is used to perform these operations.

Subsequently, the ratio "C" of the height of the centre line to the average height of the hyperfine lines is calculated. This ratio is sensitive to the value of the "effective Bohr Radius" a^* , and is particularly easy to determine experimentally.

CHAPTER IV

EXPERIMENTAL METHODS AND RESULTS

A. Apparatus and Operating Conditions

The gross features of the ESR spectrometer employed are seen in Figure 9. The klystron is a Varian Associates reflex type, delivering approximately 70 mW. over the frequency range 8.5 to 10GHz. The klystron frequency was stabilized by a standard automatic frequency control (AFC) that was "locked" to an external cavity of high Q and variable frequency, enabling observation in the dispersive mode. If we consider the equivalent circuit to a resonant cavity, X' is proportional to the change in resonant frequency of the cavity as the resonant condition is swept through. It was found that the most sensitive position of the external cavity was approximately one half way up the resonant cavity as shown:

Figure 10. Mode shape and sample cavity.

where the change in reflected power (which is monitored by the crystal detector) per unit change in cavity frequency will presumably be maximum.

The brass cavity used was designed to operate in the TE_{102} mode and was gold plated by an immersion type gold plating solution. Aluminum foil wrapped around its exterior excluded any optical light,

and two pyrex filters situated in the waveguide just above the coupling hole shielded the sample from infra-red radiation¹. Fairly consistent semi-critical coupling to the cavity was achieved as long as these filters were at least 1 cm. above the coupling hole. The samples used had dimensions $\sim 10 \times 4 \times 4$ mm. and were held to the centre of the bottom of the cavity by vacuum grease.

Low temperatures were achieved by pumping on liquid He⁴ that was transferred into an inner dewar containing the resonant cavity and waveguide. The pump used had a 150 cubic ft./min. capacity, and pumped on a 6" line. Temperatures achieved were found to be consistently close to 1.05°K during the course of the experiments.

Field modulation coils that enabled observation of the derivative of the dispersion were operated at 400Hz and amplitude .5 Oersteds. The input to these coils also served as the reference for the lockin amplifier, to which was fed the output of the crystal preamplifier. The static magnetic field was provided by a Newport Instruments 8" electromagnet with variable sweep control.

Block Diagram of Experimental Apparatus

B. Experimental Results

The ESR spectrum was obtained at 1.05°K for four samples with concentrations of .8, 1.7, 2.3 and 3.7×10^{16} donors / cm^3 . A typical spectra for $\text{Nd} = 4 \times 10^{16} / \text{cm}^3$ is shown in Figure 1. The experimental ration C of the centre line height to average hyperfine line height was plotted as seen in Figure 12. The theoretical ratio using an assumed effective Bohr radius a^* was then calculated, and the best fit of the experimental results was obtained for $a^* = 17.3\text{\AA}$. This theoretical ratio is seen as the solid line in Figure 12. Using this value of a^* and the theoretical spectrum C was calculated to be 20.2 % for a $\text{Nd} = 3.7 \times 10^{16}$ donors/ cm^3 sample at 4.2°K . This is in good agreement with the experimental value of $20 \pm 2\%$. Using this best fit value of $a^* = 17.3\text{\AA}$, $N(J)$ curves were then calculated for $\text{Nd} = 4 \times 10^{16} / \text{cm}^3$ and $6 \times 10^{16} / \text{cm}^3$, and are presented in Figure 13.

FIGURE 11

Experimental ESR Derivative Trace for $\text{Nd} = 3.7 \times 10^{16} / \text{cm}^3$

FIGURE 12

A Plot of Experimental Points and Theoretically Calculated Values of the Ratio $C(\%)$ of the Central Pair Line Intensity to the Average Intensity of the Hyperfine Lines. The Line Represents the Calculated Ratio for an Effective Bohr Radius $a^*=17.3\text{\AA}$.

FIGURE 13

A Plot of the Normalized Distribution of Pair J Values $N(J)/N_0/2$ as a Function of the Exchange Energy J for a 4×10^{16} Donors /cm³ Sample (Solid Curve) and a 6×10^{16} Donors /cm³ Sample (Dashed Curve)

C. Possible Error

The measurement of the sample concentrations were made through a standard four point probe resistivity technique. These measurements had a possible error of $\pm 5\%$, which, together with possible experimental errors in measuring the ratio, are reflected by the error bars in Figure 12. Values of a^* were then fitted to the limits of these error bars to define the accuracy of a^* . We thus obtained $a^* = 17.3A^{0+} - .2A^0$.

Additional errors may be due to a change in passage conditions from hyperfine to centre lines due to the more highly coupled and consequently faster relaxing pair systems that contribute to the centre line. We therefore changed several parameters of the observation mode, notably the sweep rate and magnetic field modulation frequency, which was varied from 30 Hz to 3000 Hz. Within experimental error the resulting values of the ratio were found to be independent of these changes in observation parameters.

It was also found that the ratio "C" was significantly increased for higher microwave powers. This can be attributed to a spin diffusion phenomena³ that would increase the faster relaxing centre line absorption at the expense of the more slowly relaxing hyperfine lines. To avoid such difficulties the ratio C was measured at the lowest microwave powers consistent with useable signal to noise.

CHAPTER V

DISCUSSION OF RESULTS

The experimentally determined effective Bohr radius $a^*=17.3A^0$ is very close to $17.2A^0$, which is the arithmetic mean of the longitudinal and transverse effective Bohr radii of the anisotropic ground state impurity wavefunction¹². This agreement would seem to indicate that the effective Bohr radius in overlap calculations should be set equal to such an arithmetic mean rather than a geometric mean which has been used in previous calculations¹³.

Jerome and Winter¹⁴ via Endor techniques obtained the most probable value of J in a $P-Si$ sample where $N_d=6 \times 10^{16}/cm^3$ as 1.34×10^4 MHz. From Figure 13 which presents our normalized $N(J)$ for a similar sample, the most probable value of J is seen to be 50 MH. Part of this discrepancy may be due to the complications introduced into the interpretation of Endor results due to the J dependent electronic spin lattice relaxation time. But more importantly, it might be pointed out that Endor measurements only involved those parts for which $J \geq A$, thus ignoring the great bulk of more weakly coupled pairs.

In conclusion, the excellent agreement that is achieved between the calculated and experimental results (Figure 13) provides confidence in the isotropic assumption of the effective Bohr radius, and also in our assumption of a random distribution of impurities. This unified, self consistent approach should provide useful and detailed information on the distribution of exchange coupled pairs which has hitherto been unavailable.

BIBLIOGRAPHY

1. Slichter, C.P., Phys. Rev. 99, 479 (1955)
2. Marko, J.R., Phys. Lett. 27A, 119 (1968)
3. Yang, G. and Honig, A., Phys. Rev. 168, 271 (1967)
4. Pake, G.E., Paramagnetic Resonance, Ed. D. Pines, 38 (W.A. Benjamin Inc., N.Y., 1962)
5. Kohn, W., in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., N.Y., 1957), Vol. 5
6. Kohn, W. and Luttinger, J.M., Phys. Rev. 98, 915 (1955)
7. Alexander, M.N. and Holcomb, D.F., Rev. Mod. Phys. 40, 815 (1968)
8. Anderson, P.W., in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., N.Y., 1963), Vol. 14
9. Portis, A.M., Phys. Rev. 91, 1071 (1953)
10. Chandrasekhar, S., Rev. Mod. Phys. 15, 1 (1943)
11. Honig, A., Physica 24, 1635 (1958)
12. Miller, A. and Abrahams, E., Phys. Rev. 120, 745 (1960)
13. Sugihara, K., J. Phys. Chem. Solids 29, 1099 (1968)
14. Jerome, D. and Winter, J.M., Phys. Rev. 134, A1001 (1964)
15. Pauling, L. and Wilson, E.B., Introduction to Quantum Mechanics, 343 (McGraw-Hill Book Company Inc., N.Y., 1935)

APPENDIX A

POPULATION DIFFERENCES BETWEEN TRANSITION LEVELS

Our whole calculation of the spectrum is based on the fact that all the localized impurity pairs are "distinguishable". Therefore, even though the electrons are fermions, the relative populations of the various pair levels will be given by Boltzmann statistics. With reference to Figure 5, page 17, we discount the splitting of the various triplet lines (as $A \ll kH_0$) and obtain the simplified energy level diagram given in Figure 15.

Figure 15. Simplified energy level diagram of the donor pair. Therefore, if we assign a population of 1 to energy level 1, and a total population of N to the whole system, the fractional populations of the other states are given by:

$$\text{State 1. } N_1 = \frac{N e^{-\beta E_1}}{\sum_i e^{-\beta E_i}} \equiv 1 \quad (\text{A-1-1})$$

$$\text{thus: } \sum_i e^{-\beta E_i} = N e^{-\beta E_1} \quad (\text{A-1-2})$$

$$\text{State 2. } N_2 = \frac{N e^{-\beta E_2}}{\sum_i e^{-\beta E_i}} = e^{\beta(E_1 - E_2)} \quad (\text{A-1-3})$$

and similarly for states 3 and 4. The results of this calculation and corresponding population differences are given in Table V.

TABLE V

Boltzmann Population Differences Between Transition Levels

Transition	Population Difference $f_B(J, \Delta, T)$
15 $\rightarrow$ 8 14 $\rightarrow$ 7	$\exp\left[-\frac{(J + \sqrt{J^2 + A^2})}{2kT}\right] \left\{ \exp\left[\frac{\delta H_0}{kT}\right] - 1 \right\}$
7 $\rightarrow$ 2 8 $\rightarrow$ 3	$\exp\left[-\frac{(J + \sqrt{J^2 + A^2})}{2kT}\right] \left\{ 1 - \exp\left[-\frac{\delta H_0}{kT}\right] \right\}$
11 $\rightarrow$ 15 12 $\rightarrow$ 14	$\left \left(1 - \exp\left[\frac{2\delta H_0 - J - \sqrt{J^2 + A^2}}{2kT}\right] \right) \right $
12 $\rightarrow$ 2 11 $\rightarrow$ 3	$1 - \exp\left[-\frac{(2\delta H_0 + J + \sqrt{J^2 + A^2})}{2kT}\right]$
16 $\rightarrow$ 9 13 $\rightarrow$ 5	$\exp\left[-\frac{(J + \sqrt{J^2 + A^2})}{2kT}\right] \left\{ \exp\left[\frac{\delta H_0}{kT}\right] - 1 \right\}$

APPENDIX B

CALCULATION OF EXCHANGE

The term J_{12}^0 of equation 1-10 is now to be calculated explicitly.

Substituting the shielded potential $-e^2/\kappa r_{12}$ seen by the donor electrons for the hydrogenic potential $-e^2/r_{12}$, and writing

$\underline{r} = \underline{r}_2 - \underline{r}_1$ we obtain:

$$J_{12}^0 = \frac{e^2}{\kappa} \int \psi_1^*(\underline{r}_1 - \underline{r}) \psi_2(\underline{r}_2) \left\{ \int \psi_2^*(\underline{r}_1 + \underline{r}) \psi_2(\underline{r}_1) d\underline{r}_1 \right\} d\underline{r}_2 \quad (A-2-1)$$

As

$$\psi_1(\underline{r}) = F(\underline{r}) \sum_n a_n e^{i \underline{k}_0^{(n)} \cdot \underline{r}} u_{\underline{k}_0^{(n)}}(\underline{r})$$

J_{12}^0 can now be written:

$$J_{12}^0 = \frac{e^2}{\kappa} \int F(\underline{r}_2 - \underline{r}) F(\underline{r}_2) \sum_{n, n'} a_n a_{n'} e^{-i \underline{k}_0^{(n)} \cdot (\underline{r}_2 - \underline{r})} e^{i \underline{k}_0^{(n')} \cdot \underline{r}_2} u_{\underline{k}_0^{(n)}}(\underline{r}_2 - \underline{r}) u_{\underline{k}_0^{(n')}}(\underline{r}_2) \\ \left\{ \int \frac{F_2(\underline{r}_1 + \underline{r}) F(\underline{r}_1)}{r} \sum_{n'', n'''} a_{n''} a_{n'''} e^{-i \underline{k}_0^{(n'')} \cdot (\underline{r}_1 + \underline{r})} e^{i \underline{k}_0^{(n''')} \cdot \underline{r}_1} u_{\underline{k}_0^{(n'')}}(\underline{r}_1 + \underline{r}) u_{\underline{k}_0^{(n''')}}(\underline{r}_1) d\underline{r}_1 \right\} d\underline{r}_2 \quad (A-2-2)$$

We examine the inner integral given by $\left\{ \right\}$. Using the periodicity of the u 's ($u_{\underline{k}_0^{(n''')}}(\underline{r}_1 + \underline{r}) = u_{\underline{k}_0^{(n''')}}(\underline{r})$)

$$\left\{ \right\} = \sum_{n'', n'''} a_{n''} a_{n'''} e^{-i \underline{k}_0^{(n'')} \cdot \underline{r}} \int \frac{F_2(\underline{r}_1 + \underline{r}) F(\underline{r}_1)}{r} e^{i (\underline{k}_0^{(n''')} - \underline{k}_0^{(n'')}) \cdot \underline{r}_1} u_{\underline{k}_0^{(n'')}}(\underline{r}) u_{\underline{k}_0^{(n''')}}(\underline{r}) d\underline{r}_1 \quad (A-2-3)$$

As $u_{\underline{k}_0^{(n'')}}(\underline{r}_1) u_{\underline{k}_0^{(n''')}}(\underline{r}_1)$ is periodic in $\underline{r}_1$, we expand it in a Fourier series:

$$u_{\underline{k}_0^{(n'')}}(\underline{r}_1) u_{\underline{k}_0^{(n''')}}(\underline{r}_1) = \sum_{\underline{y}} B_{n'' n'''}^{\underline{y}} e^{-i \underline{K}_{\underline{y}} \cdot \underline{r}_1} \quad (A-2-4)$$

Thus:

$$\left\{ \right\} = \sum_{n'', n'''} a_{n''} a_{n'''} e^{-i \underline{k}_0^{(n'')} \cdot \underline{r}} \left(\sum_{\underline{y}} B_{n'' n'''}^{\underline{y}} \int \frac{F_2(\underline{r}_1 + \underline{r}) F(\underline{r}_1)}{r} e^{i (\underline{k}_0^{(n''')} - \underline{k}_0^{(n'')} - \underline{K}_{\underline{y}}) \cdot \underline{r}_1} d\underline{r}_1 \right) \quad (A-2-5)$$

Then, if $U = \frac{F_2(\underline{r}_1 + \underline{r}) F(\underline{r}_1)}{r}$ varies slowly with $\underline{r}_1$, (this is

equivalent to the "gentle potential approximation"⁵ basic to the derivation of the impurity wavefunctions) one can obtain:

$$\int U e^{i(\underline{k}_0^{(n''')} - \underline{k}_0^{(n'')} - \underline{K}) \cdot \underline{r}} d\underline{r} \xrightarrow{\left(\lim_{\Delta U \rightarrow 0} \frac{\Delta U}{\Delta \underline{r}}\right)} (\text{const}) \delta |\underline{k}_0^{(n''')} - \underline{k}_0^{(n'')} - \underline{K}| \quad (\text{A-2-6})$$

by using the common definition of the delta function.

As $\underline{k}_0^{(n''')}$ and $\underline{k}_0^{(n'')}$ are both in the first Brillouin zone, and $\underline{K}$ is a reciprocal lattice vector, equation A-2-6 demands $\underline{K} = 0$ or $\underline{r} = 0$ for non-negligible contributions in this gentle potential limit. Similarly, $\underline{k}_0^{(n''')}$ and $\underline{k}_0^{(n'')}$ must be in the same direction in order that their difference be close to zero, which provides the condition $n''' = n''$. Therefore

$$\left\{ \right\} = \sum_{n''} \alpha_{n''}^2 e^{-i \underline{k}_0^{(n'')} \cdot \underline{r}} \int \frac{F_2(\underline{r}_1 + \underline{r}) F_1(\underline{r}_1) d\underline{r}_1}{r} \quad (\text{A-2-7})$$

where the orthonormality of the $u_{\underline{k}_0^{(n)}}(\underline{r})$'s has been used to obtain

$$B_{n'', n'''}^0 = 1.$$

Thus

$$J_{12}^0 = \sum_{n''} \alpha_{n''}^2 e^{-i \underline{k}_0^{(n'')} \cdot \underline{r}} \iint \frac{F_1(\underline{r}_2 - \underline{r}) F_2(\underline{r}_2) F_2(\underline{r}_1 + \underline{r}) F_1(\underline{r}_1)}{r} \quad (\text{A-2-8})$$

$$\cdot \sum_{n, n'} \alpha_n \alpha_{n'} e^{i \underline{k}_0^{(n)} \cdot \underline{r}} e^{i(\underline{k}_0^{(n')} - \underline{k}_0^{(n)}) \cdot \underline{r}} u_{\underline{k}_0^{(n)}}(\underline{r}_1) u_{\underline{k}_0^{(n')}}(\underline{r}_1) d\underline{r}_1 d\underline{r}_2$$

which, by the same type of procedure can be written as

$$J_{12}^0 = \sum_{n, n'} \frac{\alpha_n^2 \alpha_{n'}^2}{K} e^{i(\underline{k}_0^{(n)} - \underline{k}_0^{(n')}) \cdot \underline{r}} \cdot e^2 \iint \frac{F_1(\underline{r}_1) F_2(\underline{r}_2) F_2(\underline{r}_2) F_1(\underline{r}_1)}{r} d\underline{r}_1 d\underline{r}_2 \quad (\text{A-2-9})$$

Noting that the F_1 's, F_2 's are hydrogenic 1s wavefunctions with an effective Bohr radius a^* , the integral K is recognized to be equivalent to the integral K' evaluated by Pauling and Wilson¹⁵ in a treatment of the hydrogen molecule, where $a = a^*$. They obtain

$$K = \frac{e^2}{a^*} \left[-e^{-2D} \left(-\frac{25}{8} + \frac{23}{4} D + 3D^2 + \frac{1}{3} D^3 \right) + \frac{6}{D} \left\{ \Delta^2 (\gamma + \ln D) + \Delta'^2 E_i(-4D) - 2\Delta\Delta' E_i(-2D) \right\} \right] \quad (A-2-10)$$

where

$$D = r/a^*$$

$$\gamma = .57722$$

$$\Delta = e^{-D} (1 + D + D^2/3)$$

By an exactly similar analysis, using 42-10, 42-12 of Pauling and Wilson¹⁵:

$$S_{12} = \sum_n \alpha_n^2 e^{i \mathbf{k}_0^{(n)} \cdot \mathbf{r}} \Delta \quad (A-2-11)$$

and

$$L_{12} = \sum_{n, n'} \alpha_{n'}^2 e^{-i \mathbf{k}_0^{(n')} \cdot \mathbf{r}} \left(-\frac{e^2}{K} \right) e^{-D} (1 + D) \quad (A-2-12)$$

As $J_{12} = J_{12}^0 - 2 S_{12} L_{12}$, we have as our final expression:

$$J_{12} = \frac{e^2}{K a^*} \sum_{n, n'} \alpha_n^2 \alpha_{n'}^2 e^{i (\mathbf{k}_0^{(n)} - \mathbf{k}_0^{(n')}) \cdot \mathbf{r}} e^{-2D} \left\{ 2(1+D) \left(1 + D + \frac{D^2}{3} \right) - \frac{1}{5} \left\{ -\left(-\frac{25}{8} + \frac{23}{4} D + 3D^2 + \frac{1}{3} D^3 \right) + \frac{6}{D} \left[\left(1 + D + \frac{D^2}{3} \right)^2 (\gamma + \ln D) \right] \right\} \right\} \quad (A-2-13)$$

where terms $O(E_i(-2D))$ have been discounted as they go to zero very quickly for $D \gg \frac{1}{2}$.

As $|\mathbf{k}_0^{(n)}| = .85 \pi/a$, where a is the lattice spacing, for all n , the interference term in equation A-2-13 can be rewritten as:

$$\sum_{n, n'} \alpha_n \alpha_{n'} e^{i (\mathbf{k}_0^{(n)} - \mathbf{k}_0^{(n')}) \cdot \mathbf{r}} = 4 \left(\sum_n \cos(\mathbf{k}_0^{(n)} \cdot \mathbf{r}) \right)^2 \quad (A-2-14)$$

Therefore, equation A-2-13 becomes:

$$\begin{aligned} \bar{J}_{12}(r) = & \frac{1}{9} \cdot \frac{e^2}{\kappa a^*} \cdot \left(\sum_n \cos(\mathbf{k}_n^{(1)} \cdot \mathbf{r}) \right)^2 e^{-2D} \left\{ 2(1+D)\left(1+D+\frac{D^2}{3}\right) \right. \\ & \left. - \frac{1}{5} \left[-\left(-\frac{25}{8} + \frac{23}{4}D + 3D^2 + \frac{1}{3}D^3\right) + \frac{6}{D} \left[\left(1+D+\frac{D^2}{3}\right)^2 (\gamma + \ln D) \right] \right] \right\} \quad (A-2-15) \end{aligned}$$

which is our final expression.

APPENDIX C

THE DISTRIBUTION OF NEAREST EXCHANGE COUPLED PAIRS

a. Calculation of the Number of Lattice Sites in Shells of Unit Thickness Centered on the Origin.

Silicon has a so-called "diamond" crystalline structure consisting of two interlocking face-centred cubic lattices.

Figure 14. Simple Face-centred Cubic Lattice Structure (F.C.C.)

For the simple F.C.C. lattice noted in the above figure, the basic lattice transformations depicted are given by

$$\begin{aligned}\underline{a}_1 &= \frac{a}{2} (\hat{i} + \hat{j}) \\ \underline{a}_2 &= \frac{a}{2} (\hat{i} + \hat{k}) \\ \underline{a}_3 &= \frac{a}{2} (\hat{j} + \hat{k})\end{aligned}\tag{A-3-1}$$

Therefore, lattice sites are at positions $\underline{R}$ where

$$\underline{R} = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3 \text{ where } n_1, n_2, n_3 \text{ are integers.}\tag{A-3-2}$$

The second F.C.C. lattice of silicon is displaced along the body diagonal of the cube depicted in Figure 14 by $\frac{1}{4}$ of its length. Therefore the lattice points of the second lattice are described by

R where:

$$\underline{R}' = \underline{R} + \frac{a}{4} (\hat{i} + \hat{j} + \hat{k}) \quad (\text{A-3-3})$$

The distance $R = (\underline{R} \cdot \underline{R})^{\frac{1}{2}}$ of the lattice sites from the origin is then given by:

$$R = \frac{a}{2} \sqrt{(n_1 + n_2)^2 + (n_1 + n_3)^2 + (n_2 + n_3)^2} \quad (\text{A-3-4})$$

for the first lattice, and by:

$$R' = \frac{a}{2} \sqrt{(n_1 + n_2 + .5)^2 + (n_1 + n_3 + .5)^2 + (n_2 + n_3 + .5)^2} \quad (\text{A-3-5})$$

for the second lattice.

When this formulation is used in the 360-67 computer to calculate the number of lattice sites in shells of width $1 \text{ \AA}$, it becomes extremely costly in computer time to proceed past $r = 100 \text{ \AA}$. It is, however, essential to the calculation that we do so. Thus the problem was reformulated by using the symmetry properties of the lattice.

The basic quantities of interest are the absolute value of R and (for the interference term in eq. A-2-15) the projections of R on the x, y, z axes respectively. The interference term is seen to be an even function of these projections. Therefore we shall calculate the absolute value of the projections of various R on the x, y, z axes respectively and find the number of lattice sites that correspond to each set of projections. The analysis, although tedious, is conceptually trivial, and in essence consists of treating the two interlocking F.C.C. lattices as 8 interlocking cubic lattices. The resulting absolute values of the projections and corresponding lattice sites are summarized in Table VI. It was then easy to calculate the number of lattice sites contained in each shell of width $1 \text{ \AA}$, and to subsequently obtain the probability that any one site in that shell was an impurity site through equation 2-16.

TABLE VI

Number of Lattice Sites Having the Same Absolute Value for Projections on the x, y, z Axes in a Crystal With Interlocking F.C.C. Structure.

Absolute Value of Projections ($n_1, n_2, n_3 \geq 1$ where n_1, n_2, n_3 are integers)			No. of "Equivalent" Sites
x	y	z	
$n_1 a$	$(n_2 - 1)a$	$n_3 a$	8
$n_1 a$	$(n_2 - .5)a$	$(n_3 - .5)a$	24
$(n_1 - .75)a$	$(n_2 - .75)a$	$(n_3 - .25)a$	12
$(n_1 - .75)a$	$(n_2 - .25)a$	$(n_3 - .25)a$	12
$(n_1 - .75)a$	$(n_2 - .75)a$	$(n_3 - .75)a$	4
$(n_1 - .25)a$	$(n_2 - .25)a$	$(n_3 - .25)a$	4
$(n_1 - .5)a$	$(n_2 - .5)a$	0	12
$n_1 a$	$n_2 a$	0	4
$n_1 a$	0	0	6

b. Determination of the Nearest Neighbour Distribution

This was performed by Program I. The probability that a lattice site in a particular shell was a nearest donor, as calculated in Section A for a particular concentration N_d , was read in as the array P . The exchange energy J was then calculated, according to equation 1-10, for each collection of "equivalent" sites assuming an effective Bohr radius a^* ($=AD$). Subsequently, depending upon which range the $\log(J)$ term corresponds to, the probability P multiplied by the number of equivalent sites L is added to a certain element of the $F\tau\phi\tau$ array. This program is run for all the equivalent sites noted in Table VI, which entails nine separate computations in order to obtain the final discrete $F\tau\phi\tau$, or $N(J)$, array.

PROGRAM I

\$LIS THENOJ

```

1      DIMENSION RR(250),NO(250),PROB(250),ALJ(250),P(250),FTOT(250)
2      REAL LGE,JJ(250)
3      AA=2.90E08
4      BB=2./9.
5      CC=1./45.
6      ALPHA=5.3
7      E=.85*3.1416
8      LGE=ALOG10(2.71828)
9      READ (4,100) DIST,AD
10     100  FORMAT (2F10.2)
11     N=DIST
12     DO 2 I=1,N
13     READ (5,101) RR(I),NO(I),P(I)
14     101  FORMAT (F10.2,I10,E10.2)
15     NO(I)=0
16     FTOT(I)=0.
17     PROB(I)=0.
18     2    CONTINUE
19     M=INT(DIST/5.3)
20     NJMAX=90
21     NJMIN=-15
22     NN=NJMAX+16
23     READ (4,104) GOD
24     104  FORMAT (F10.2)
25     IF (GOD.EQ.0.) GO TO 8
26     DO 6 I=1,NN
27     READ (3,102) JJ(I),JJ(I+1),ALJ(I),ALJ(I+1),PROB(I)
28     6    CONTINUE
29     DO 7 I=1,N
30     READ (3,103) RR(I),NO(I),FTOT(I)
31     7    CONTINUE
32     8    CONTINUE
33     DO 1 I=1,M
34     .
35
36     A=I
37     B=0
38     C=0
39     L=6
40     R=ALPHA*SQRT(A**2+B**2+C**2)
41     IF (R.GT.DIST+1) GO TO 1
42     NR=R
43     F=(COS(E*A)+COS(E*B)+COS(E*C))**2
44     FTOT(NR)=FTOT(NR)+ALOG10(F)*L
45     NO(NR)=NO(NR)+L
46     D=R/AD
47     FD=AA*BB*(1.+D)*(1.+D+D**2/3.)*EXP(-2.*D)/AD
48     GD=AA*CC*(25./8.-5.75*D-3.*D**2-D**3/3.
49     2+(6./D)*((1.+D+D**2/3.))**2*(.57777+ALOG(D)))*EXP(-2.*D)/AD
50     X=F*(FD-GD)
51
52     NJ=INT(10.*ALOG10(X))

```

```
53      IF (NJ.LT.NJMIN) GO TO 1
54      NJ=NJ+16
55      PROB(NJ)=PROB(NJ)+L*P(NR)
56      1  CONTINUE
57      ALJ(1)=-15
58      JJ(1)=EXP(ALJ(1)/(10.*LGE))
59      ALJ(1)=-1.5
60      DO 4 I=1,NN
61      ALJ(I+1)=(I-15)/10.
62      JJ(I+1)=EXP(ALJ(I+1)/LGE)
63      WRITE (6,102) JJ(I),JJ(I+1),ALJ(I),ALJ(I+1),PROB(I)
64      WRITE (7,102) JJ(I),JJ(I+1),ALJ(I),ALJ(I+1),PROB(I)
65      4  CONTINUE
66      102  FORMAT (2E10.2,2F10.2,1PE10.2)
67      DO 5 I=1,N
68      WRITE (6,103) RR(I),NO(I),FTOT(I)
69      WRITE (7,103) RR(I),NO(I),FTOT(I)
70      5  CONTINUE
71      103  FORMAT (F10.2,I10,F20.5)
72      STOP
73      END
END OF FILE
```

A continuous approximation to this $N(J)$ distribution necessitates determining a suitable average value for the interference term in equation 1-10. As the distribution of nearest donors is calculated as a function of $\log(J)$ rather than J , we calculated $\log\left(\sum_n \cos(k_n^{(n)} \cdot r)\right)^2$, and obtained the appropriate average value of $\left(\sum_n \cos k_n^{(n)} \cdot r\right)^2$ to be .4663. Writing J as a continuous function of r , and assuming the nearest donor distribution given by equation , the probability $N(J)$ that a nearest donor pair has exchange energy in the range $J, J+dJ$ is given by:

$$N(J) dJ = \frac{4\pi N_d r^2 e^{-\frac{4\pi N_d r^3}{3}}}{(dJ/dr)} dJ \quad (A-3-6)$$

Therefore, upon integrating A-3-6 over a certain range of J (the same intervals as in the discrete calculation are used) one should obtain a reasonable approximation to the discrete distribution. This procedure is performed by Program II, where J is denoted by X , and dJ/dr by XP . The resulting probability as calculated from equation A-3-6 is entered into the array PNJ , which the second section of the program integrates over the intervals of J .

PROGRAM II

\$LIS NOJ2

```

1      C      THIS PROG. CALCS. THE FRACT. # OF NRST. DONOR PRS. HAVING
2      C      EXCHANGE ENERGY "J" FROM A POISSON DIST. OF NRST. DONORS.
3      READ (5,100) N,AD,CON,RMIN,RMAX
4      100    FORMAT (I10,F10.2,E10.2,2F10.2)
5      LOGICAL L1,L2
6
7
8      N=300
9      DIMENSION ALJ(600),PNJ(600),PJ(600)
10     DIMENSION RR(600)
11     REAL LJ(600)
12     DO 20 I=1,600
13     PNJ(I)=0.0
14     20     CONTINUE
15     AA=2.90E08
16     BB=2./9.
17     CC=1./45.
18     F=.4663
19     DELR=(RMAX-RMIN)/N
20     DO 1 I=1,N
21     R=RMIN+(I-1)*DELR
22     D=R/AD
23     FD=AA*BB*(1.+D)*(1.+D+D**2/3.)*EXP(-2.*D)/AD
24     GD=AA*CC*(25./8.-5.75*D-3.*D**2-D**3/3.+6./D*(1.+D+D**2/3.))*
25     2(.57722+ALOG(D))*EXP(-2.*D)/AD
26     X=F*(FD-GD)
27     XP=-2*X/AD+F*AA*EXP(-2.*D)/AD**2*(BB*((1+2*D/3)*(1+D)+
28     2(1+D+D**2/3))-CC*(-5.75-6*D-D**2-6/D**2*(1+D+D**2/3)**2*
29     3(-.42278+ALOG(D))+12/D*(1+D+D**2/3)*(1+2*D/3)*(.577+ALOG(D))
30     4)
31
32     ALJ(I)=ALOG10(X)
33     PNJ(I)=-4.*3.1416*CON*R**2*EXP(-4./3.*3.1416*CON*R**3)/XP
34     WRITE (7,101) R,ALJ(I),PNJ(I)
35     101    FORMAT (2F20.2,E20.5)
36     1     CONTINUE

```

```

43      PJ(1)=0.
44      DO 2 I=1,200
45      LJ(I)=(80.-I)/10.
46      DO 10 J=1,N
47      L1=LJ(I).LE.ALJ(J)
48      L2=LJ(I).GE.ALJ(J+1)
49      IF (L1.AND.L2) GO TO 11
50      10  CONTINUE
51      11  CONTINUE
52      IF (ALJ(J).EQ.0.) GO TO 21
53      PJ(I)=(LJ(I)-ALJ(J))*(PNJ(J+1)-PNJ(J))/(ALJ(J+1)-ALJ(J)
54      2)+PNJ(J)
55      GO TO 22
56      21  CONTINUE
57      PJ(I)=0.
58      22  CONTINUE
59      WRITE (6,102) I,LJ(I),PJ(I)
60      102  FORMAT (I10,F10.3,E20.5)
61      2    CONTINUE
62      STOP
63      END
64      REAL LJ(600),J(600),NJ(600),JO,LGE,LLJ(200)
65      NA=10
66
67      DIMENSION PNJ(200)
68      COMMON PNJ,LLJ
69
70
71      DO 202 I=1,200
72      READ (5,200) K,LLJ(I),PNJ(I)
73      200  FORMAT (I10,F10.3,E20.5)
74      202  CONTINUE
75
76      N=200
77      LGE=ALOG10(2.71828)
78      LJ(1)=80.
79
80      J(1)=EXP(LJ(1)/(10.*LGE))
81      AREA=0.
82      DO 1 I=1,200
83      LJ(I+1)=80-I
84      J(I+1)=EXP(LJ(I+1)/(10.*LGE))
85      CALL SIMP (J(I),J(I+1),NA,NJ(I),CON,JO,ALPHA,M,T)
86      AREA=AREA+NJ(I)
87      WRITE (6,101) J(I),J(I+1),LJ(I),LJ(I+1),NJ(I)
88      101  FORMAT (2E10.2,2F10.2,1PE10.2)
89      1    CONTINUE
90      WRITE (6,102) AREA
91      102  FORMAT (// 'AREA UNDER CURVE =',F10.4)
92      STOP
93      END

```

END OF FILE

APPENDIX D

CALCULATION OF THE THEORETICAL SPECTRUM

This calculation was performed by Program III. The basic operations involved consisted of breaking up the energy into intervals, contained in the array E, calculating the corresponding intervals of exchange energy which were entered into the array J, and subsequently integrating the expression given by equation 2-17 over these intervals of J to obtain the array A. Special attention was given to points for which $E = g\beta H_0$ and $E = g\beta H_0 \pm A/2$ as the exchange energy, written as a function of energy, suffers discontinuities at these points. The elements of the array A were then equated to the areas under the Gaussian shape functions given in equation 2-17, and the height of the hyperfine lines and centre line obtained as their convolution. The value of the ratio of centre to average hyperfine line was then obtained as RATIO. The continuous $N(J)$ curve for a particular concentration and effective Bohr radius as calculated by Program II was read into Program III as the array LLJ, PNJ.

PROGRAM III

\$LIS FINAL

```

1      LOGICAL L1,L2,L3,LX
2      DIMENSION E(802),A(802)
3      REAL J(802),JX(11),      LJ(600),JO,JH(21)
4      DATA N,NX,NH,8/20,50,50,118./
5      31  CONTINUE
6      READ (5,105) CON ,JO,ALPHA,AD,RMAX,T
7      IF (CON.EQ.0.E0) GO TO 30
8      DIMENSION PNJ(200)
9      REAL LLJ(200)
10     COMMON PNJ,LLJ
11     DO 202 I=1,200
12     READ (4,201) K,LLJ(I),PNJ(I)
13     202 CONTINUE
14     201 FORMAT (I10,F10.3,E20.5)
15     105 FORMAT (2E10.2,4F10.4)
16     DO 1 I=1,802
17     E(I)=9799.5+FLOAT(I)*.5
18     IF (E(I).EQ.1.E 04) GO TO 2
19     J(I)=ABS(B**2/(4.*(E(I)-1. E 04))-E(I)+1.E04)
20     GO TO 7
21     2   J(I)=EXP(LLJ(1)/ALOG10(2.71828))
22     7   CONTINUE
23     E(I)=E(I)+.25
24     1   CONTINUE
25     J(283)=EXP(LLJ(200)/ALOG10(2.71828))
26     J(519)=J(283)
27     DO 3 I=1,802
28     L1=E(I).GE.9941.
29     L2=E(I).GE.10000.
30     L3=E(I).GE.10059.
31     IF (.NOT.L1) M=1
32     IF (L1.AND..NOT.L2) M=2
33     IF (L2.AND..NOT.L3) M=3
34     IF (L3) M=4
35     LX=(I.EQ.282).OR.(I.EQ.283).OR.(I.EQ.400).OR.(I.EQ.401)
36     2.OR.(I.EQ.518).OR.(I.EQ.519)
37     IF (LX) GO TO 5
38     CALL SIMP (J(I),J(I+1),N,A(I),CON,JO,ALPHA,M,T)
39     GO TO 3
40     5   A(I)=0.
41     JX(1)=AMIN1(J(I),J(I+1))
42     DO 10 K=1,10
43     X=ALOG(AMAX1(J(I),J(I+1))/AMIN1(J(I),J(I+1)))*FLOAT(K)/10.
44     JX(K+1)=AMIN1(J(I),J(I+1))*EXP(X)
45     CALL SIMP (JX(K),JX(K+1),NX,AX,CON,JO,ALPHA,M,T)
46     A(I)=A(I)+AX
47     10  CONTINUE
48     3   CONTINUE
49     HYP=0.
50     JH(1)=J(283)

```



```

51      DO 11 K=1,20
52      X=ALOG(J(401)/J(283))*FLOAT(K)/20.
53      JH(K+1)=J(283)*EXP(X)
54      CALL SIMP (JH(K),JH(K+1),NH,AH,CON,JO,ALPHA,5,T)
55      HYP=HYP+AH
56 11    CONTINUE
57      HHBL=0.
58      DO 12 I=263,303
59      HHBL=HHBL+A(I)/(SQRT(2.*3.1416)*8.)*EXP(-.5*((E(283) -E(I))/8.))**2
60      2)
61 12    CONTINUE
62      HCL=0.
63      DO 13 I=381,421
64      HCL=HCL +A(I)/(SQRT(2.*3.1416)*8.)*EXP(-.5*((E(401) -E(I))/8.))**2
65      2)
66 13    CONTINUE
67      HHBR=0.
68      DO 14 I=499,539
69      HHBR=HHBR+A(I)/(SQRT(2.*3.1416)*8.)*EXP(-.5*((E(519) -E(I))/8.))**2
70      2)
71 14    CONTINUE
72      HHL=HYP/(SQRT(2.*3.1416)*8.)
73      RATIO=2.*HCL/(2.*HHL+HHBL+HHBR)*100.
74      HL=HHL+HHBL
75      HR=HHL+HHBR
76      WRITE (6,100) AD,JO,ALPHA,CON,T,RMAX
77      WRITE (6,102) N,NX,NH,HL ,HCL,HR
78      WRITE (6,103) RATIO
79      GO TO 31
80 30    CONTINUE
81      STOP
82 100    FORMAT (///55X,'AD=',F5.1,///1X,'JO=',E10.2,9X,'ALPHA=',
83 2F10.3,7X,'CON=',E10.2,9X,'TEMP=',F10.2,8X,'RMAX=',F10.1/)
84 102    FORMAT (/50X,'CHECKING PARAMETERS',//1X,'N=',I8,38X,'NH=',
85 2I8,38X,'NH=',I8,//2X,'HEIGHT OF LEFT HYPERFINE LINE =',1PE10.2,
86 3/2X,'HEIGHT OF CENTRE LINE =',8X,E10.2,/2X,
87 4'HEIGHT OF RIGHT HYPERFINE LINE =',E10.2/)
88 103    FORMAT (/2X,'RATIO OF CENTRE LINE TO HYP LINES (BY PERCENT)
89 2 ) =',F10.2,///)
90      END
91      SUBROUTINE SIMP (A,B,N,AREA,CON,JO,ALPHA,M,T)
92      REAL JO
93      REAL LLJ(200)
94      DIMENSION PNJ(200)
95      COMMON PNJ,LLJ
96      AN = N
97      H=(B-A)/AN
98      SUM1=0.0
99      SUM2=0.0
100     CALL AUX (A,Y,CON,JO,ALPHA,M,T)
101     YA=Y
102     CALL AUX (B,Y,CON,JO,ALPHA,M,T)
103     YB=Y
104     X = A-H
105     NN=N/2
106     DO 30 I = 1,NN
107     X = X+2.0*H
108     CALL AUX (X,Y,CON,JO,ALPHA,M,T)
109 30    SUM1=SUM1+Y
110     X=A

```

```

111      DO 40 I = 2,NN
112      X = X+2.0*H
113      CALL AUX (X,Y,CON,JO,ALPHA,M,T)
114      40  SUM2=SUM2+Y
115      AREA = H/3.0*(YA+4.0*SUM1+2.0*SUM2+YB)
116      AREA=ABS(AREA)
117      RETURN
118      END
119      SUBROUTINE AUX (X,Y,CON,JO,ALPHA,M,T)
120      REAL JO ,MINUS
121      DATA BOL,AH/2.08E4,118./
122
123      REAL LLJ(200)
124      DIMENSION PNJ(200)
125      COMMON PNJ,LLJ
126      ALX=ALOG10(X)
127      IF (ALX.LT.0.) GO TO 300
128      N=80-INT(10.*ALX)
129      IF (N.LE.1) GO TO 302
130      GO TO 301
131      300  CONTINUE
132      N=81-INT(10.*ALX)
133      IF (N.GT.200) GO TO 302
134      GO TO 301
135      302  CONTINUE
136      PJ=0.0
137      GO TO 303
138      301  CONTINUE
139      PJ=-10.*(ALX-LLJ(N-1))*(PNJ(N)-PNJ(N-1))+PNJ(N-1)
140      303  CONTINUE
141      RT=SQRT(X**2+AH**2)
142      PLUS=.5*(1.+X/RT)
143      MINUS=.5*(1.-X/RT)
144      IF (M.GE.2) GO TO 2
145      Y=MINUS*PJ*ABS(1.-EXP((2.E4-X-RT)/(2.*BOL*T)))
146      GO TO 1
147      2    CONTINUE
148      IF (M.GE.3) GO TO 3
149      Y=PLUS*PJ*EXP(-(X+RT)/(2.*BOL*T))*(1.-EXP(-1.E4/(BOL*T)))
150      GO TO 1
151      3    CONTINUE
152      IF (M.GE.4) GO TO 4
153      Y=PLUS*PJ*EXP(-(X+RT)/(2.*BOL*T))*(EXP(1.E4/(BOL*T))-1.)
154      GO TO 1
155      4    CONTINUE
156      IF (M.EQ.5) GO TO 5
157      Y=MINUS*PJ*(1.-EXP(-(2.E4+X+RT)/(2.*BOL*T)))
158      GO TO 1
159      5    CONTINUE
160      Y=.5*PJ*EXP(-(X+RT)/(2.*BOL*T))
161      2*(EXP(1.E4/(BOL*T))-EXP(-1.E4/(BOL*T)))
162      1    CONTINUE
163      RETURN
164      END

```

END OF FILE