

## The Evaluation of Matrix Elements of the High-Resolution NMR Spin-Coupling Hamiltonian Using a Digital Computer<sup>1</sup>

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The calculation of matrix elements of the NMR spin Hamiltonian

$$\mathcal{H} = (2\pi)^{-1} \sum_i \gamma_i H_i I_z(i) + \sum_{i < j} J_{ij} \mathbf{I}(i) \cdot \mathbf{I}(j) \quad (1)$$

between basic state wavefunctions is one of the preliminary steps for the detailed analysis of high-resolution NMR spectra [1]. Since each basic product function is itself an eigenfunction of each term in the first part of Eq. (1), the external-field Hamiltonian, the diagonal matrix elements of this part are simply obtained by replacing  $I_z(i)$  in this part by  $\pm \frac{1}{2}$  according as the corresponding spin function is  $\alpha$  or  $\beta$ ; and there are no off-diagonal matrix elements of external-field Hamiltonian between the basic product functions. There will however, be both diagonal and off-diagonal matrix elements of second part of equation (1), the spin-coupling Hamiltonian, between the basic product functions. Moreover, in the evaluation of the matrix elements of the spin coupling Hamiltonian with five or more spin, there is considerable labor and tedious work involved. Corio [2] has proposed a method to simplify the calculations, but the calculations still must be done manually. Swalen and Reilly [8] have developed a computer subroutine for calculating these matrix elements in their iterative scheme for analysis of NMR spectra, however their program does not give these matrix elements explicitly and it cannot be used in other schemes for analysis of NMR spectra. A new method which employs a digital computer to evaluate the matrix elements of the spin coupling Hamiltonian is proposed.

If the nuclei were actually independent, the basic product function would [aside from degeneracy, which in the case of two identical nuclei, yields  $\frac{1}{2}(\alpha\beta \pm \beta\alpha)$ ] themselves be stationary-state wavefunctions (or basic state wavefunctions) in

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the presence of the external magnetic field. However, the spin-coupling Hamiltonian

$$\mathcal{H}^{(1)} = \sum_{i < j} J_{ij} \mathbf{I}(i) \cdot \mathbf{I}(j)$$

may cause mixing between different product functions. Since the basic product functions  $\psi_n$  are all orthogonal to one another, the correct stationary-state wavefunctions (or basic state wavefunctions) are the linear combinations of the basic product functions which diagonalize the matrix of the complete Hamiltonian [see Eq. (1)]. We define  $J$  as the number of basic state wavefunctions,  $K$  as the number of basic product functions in a basic state wavefunction due to degeneracy,  $L$  as the number of spin functions and  $N$  as the total number of spins. Then, spin functions, basic product functions, and basic state wavefunctions can be denoted by a three-dimension array  $ID(J, K, L)$ , e.g. in a two spin system,  $ID(1, 1, 1)$  means the first spin function in the first product function of the first-state wavefunction, that is  $\alpha$ .  $ID(2, 2, 1)$  means the first spin function in the second product function of the second-state wavefunction, i.e.,  $\beta$ . So, in the two spin system,  $\psi_1 = \alpha\alpha$  can be represented by

$$\begin{aligned} \psi_1 &= ID(1, 1, 1) ID(1, 1, 2); & \psi_2 &= 1/\sqrt{2}(\alpha\beta + \beta\alpha) \quad \text{by} \\ \psi_2 &= 1/\sqrt{2}\{ID(2, 1, 1) ID(2, 1, 2) + ID(2, 2, 1) ID(2, 2, 2)\}, \dots \text{etc.} \end{aligned}$$

The coefficients are introduced as  $CD(J, K)$ .

From the simple rules for evaluating the matrix elements [1], [3], we know that matrix elements of

$$\mathbf{I}_s \cdot \mathbf{I}_t = I_{sx}I_{tx} + I_{sy}I_{ty} + I_{sz}I_{tz}$$

exist only when the two basic product functions  $ID(J, K, L)$ ,  $L = 1, \dots, N$  i.e.  $(ID_{JK_1}ID_{JK_2} \dots ID_{JK_N})$  and  $ID(J', K', L')$ ,  $L' = 1, \dots, N$ ,

$$[\text{i.e., } (ID_{J'K'_1}ID_{J'K'_2} \dots ID_{J'K'_N})]$$

differ by no more than two of the  $ID$ 's. For computer calculation, we let these  $ID$ 's have numerical values 1 or 2 according as  $ID$ 's are  $\alpha$  or  $\beta$  spins. For example, if a basic product function is  $(ID_{JK_1}ID_{JK_2}ID_{JK_3}ID_{JK_4}) = \alpha\beta\alpha\beta$ , then it has the numerical value 1212. If another basic product function is

$$(ID_{J'K'_1}ID_{J'K'_2}ID_{J'K'_3}ID_{J'K'_4}) = \alpha\alpha\beta\alpha,$$

then it has the numerical value 1121. These two wavefunctions differ by three of the  $ID$ 's ( $ID_{JK_2} \neq ID_{J'K'_2}$ ,  $ID_{JK_3} \neq ID_{J'K'_3}$ ,  $ID_{JK_4} \neq ID_{J'K'_4}$ ) so there are no matrix elements between these two product functions. Also if the two product functions differ by one of the  $ID$ 's only, there are still no matrix elements between them. For example,  $(ID_{JK_1}ID_{JK_2}ID_{JK_3}ID_{JK_4}) = \alpha\beta\alpha\beta = 1212$ , and

$$(ID_{J'K'_1}ID_{J'K'_2}ID_{J'K'_3}ID_{J'K'_4}) = \alpha\beta\alpha\alpha = 1211$$

differ by one  $ID$  only ( $ID_{JK_4} \neq ID_{J'K'_4}$ , the other  $ID$ 's in these two product functions are the same), so there are no matrix elements between them. Matrix elements exist between two wavefunctions for even differences up to two (namely, zero and two) of the spin functions; e.g.,  $(ID_{JK_1}ID_{JK_2}ID_{JK_3}ID_{JK_4}) = \alpha\beta\alpha\beta = 1212$  and  $(ID_{J'K'_1}ID_{J'K'_2}ID_{J'K'_3}ID_{J'K'_4}) = \alpha\beta\alpha\beta = 1212$  have zero difference, so matrix elements exist between them.  $(ID_{JK_1}ID_{JK_2}ID_{JK_3}ID_{JK_4}) = \alpha\beta\alpha\beta = 1212$  and  $(ID_{J'K'_1}ID_{J'K'_2}ID_{J'K'_3}ID_{J'K'_4}) = \alpha\beta\beta\alpha = 1221$  differ by two  $ID$ 's ( $ID_{JK_3} \neq ID_{J'K'_3}$  and  $ID_{JK_4} \neq ID_{J'K'_4}$ ), so matrix elements also exist between these two basic product functions.

From the above, we know that the typical term of the matrix elements of the spin coupling Hamiltonian is  $J_{ij}\mathbf{I}(i) \cdot \mathbf{I}(j)$ , in which only two nuclei are involved. So when we calculate the matrix elements, we need only consider two nuclei each time and Table I can be easily obtained. Using the numerical characteristics of each two pairs of spin functions, Table II can be constructed. Based on Table II, the Fortran computer program<sup>1</sup> Matrel have been written for the Control Data 3600 computer.

The program used for calculation of spin-coupling-Hamiltonian matrix elements is quite straightforward. The basic state wavefunctions, the basic product functions and spin functions are numbered by  $J$ 's,  $K$ 's, and  $L$ 's, respectively. The program steps systematically through all of the basic wavefunctions, attempting to calculate the matrix element between each different pair of basic state wavefunctions. First it calculates the matrix element between  $\psi_1$  and  $\psi_1$ , then  $\psi_1$  and  $\psi_2$ , then  $\psi_1$  and  $\psi_3$ , ... to  $\psi_{JL}$ , which is the last of the basic state wavefunctions; then it comes back to calculate  $\psi_2$  and  $\psi_1$ ,  $\psi_2$  and  $\psi_2$ , and so forth. The computer picks up two basic state wavefunctions  $\psi_1$  and  $\psi_1$ , then compares the basic product functions in the basic state wavefunctions (e.g., it compares the basic product function of  $J = 1, K = 1$  with that of  $J = 1, K = 1$ ; then  $J = 1, K = 1$  with  $J = 1, K = 2$ ; then  $J = 1, K = 2$  with  $J = 1, K = 1$ ; then  $J = 1, K = 2$  with  $J = 1, K = 2$ ). If these two basic product wavefunctions have matrix elements between them, then the computer goes further to pick up each different pair of spin functions and performs various tests as listed in the Table II, classifies it into one of the eight cases in Table II, and gives a value for the coefficient of the spin coupling constant of these two nuclei. If these two basic product wavefunctions do not differ (i.e., have the same spin wavefunction) the computer also assigns a value according to Table II for the coefficients of the spin-coupling constant of any two nuclei. If these two basic products do not have matrix elements, then the computer picks up another basic product function for comparison. These procedures go on and on until it has calculated all the possible matrix elements. The output will be all the coefficients of all the spin-coupling constants; e.g., in five-spin

<sup>1</sup> Fortran Listings for the computer programs can be obtained from the authors.

TABLE I

$(ID_{JKS}ID_{JKt})$	$(ID_{JK'S}ID_{JK't})$	Coefficient for $J_{st}I_{sz}I_{tz}$	+	Coefficient for $J_{st}I_{sy}I_{ty}$	+	Coefficient for $J_{st}I_{sz}I_{tz}$	=	Total coeff. for $J_{st}I_{sz} \cdot I_t$
$\alpha \alpha$	$\alpha \alpha$	0	+	0	+	1/4	=	1/4
$\alpha \beta$	$\alpha \beta$	0	+	0	+	(-1/4)	=	-1/4
$\beta \alpha$	$\beta \alpha$	0	+	0	+	(-1/4)	=	-1/4
$\beta \beta$	$\beta \beta$	0	+	0	+	1/4	=	1/4
$\alpha \alpha$	$\beta \beta$	1/4	+	(-1/4)	+	0	=	0
$\beta \beta$	$\alpha \alpha$	1/4	+	(-1/4)	+	0	=	0
$\alpha \beta$	$\beta \alpha$	1/4	+	1/4	+	0	=	1/2
$\beta \alpha$	$\alpha \beta$	1/4	+	1/4	+	0	=	1/2

TABLE II

Case	Coef. for $J_{st}$	$ID_{JKS}ID_{JKt}$	$ID_{JK'S}ID_{JK't}$	$ID_{JKS} - ID_{JK't}$	$ID_{JKt} - ID_{JK't}$	$ND(S) = ID_{JKS} - ID_{JK't}$	$ND(t) = ID_{JKt} - ID_{JK't}$	$NABS =  ND(S)  +  ND(t) $	$NDD = ND(S) - ND(t)$	$NSUM = ND(S) + ND(t)$	Both $ID_{JKS}$ and $-ID_{JKt}$ Pairs
$I_a$	1/4	$\alpha \alpha$	$\alpha \alpha$	1 - 1 = 0	1 - 1 = 0	1 - 1 = 0	1 - 1 = 0	0	0	0	same
$I_b$	-1/4	$\alpha \beta$	$\alpha \beta$	1 - 1 = 0	2 - 2 = 0	2 - 2 = 0	2 - 2 = 0	0	0	0	same
$I_c$	-1/4	$\beta \alpha$	$\beta \alpha$	2 - 2 = 0	1 - 1 = 0	1 - 1 = 0	1 - 1 = 0	0	0	0	same
$I_d$	1/4	$\beta \beta$	$\beta \beta$	2 - 2 = 0	2 - 2 = 0	2 - 2 = 0	2 - 2 = 0	0	0	0	same
$0_a$	0	$\alpha \alpha$	$\beta \beta$	1 - 2 = -1	1 - 2 = -1	1 - 2 = -1	1 - 2 = -1	2	0	-2	diff.
$0_b$	0	$\beta \beta$	$\alpha \alpha$	2 - 1 = 1	2 - 1 = 1	2 - 1 = 1	2 - 1 = 1	2	0	2	diff.
$II_a$	1/2	$\alpha \beta$	$\beta \alpha$	1 - 2 = -1	2 - 1 = 1	2 - 1 = 1	2 - 1 = 1	2	-2	0	diff.
$II_b$	1/2	$\beta \alpha$	$\alpha \beta$	2 - 1 = 1	1 - 2 = -1	1 - 2 = -1	1 - 2 = -1	2	2	0	diff.

system, the matrix element between  $\psi_1$  and  $\psi_1$  will be represented by coefficients of  $J_{ij}$  in  $J_{11}J_{12}J_{13}J_{14}J_{15}$ ,  $J_{21} \dots J_{25}$ ,  $J_{31} \dots J_{35}$ ,  $J_{41} \dots J_{45}$ ,  $J_{51} \dots J_{55}$ , and here obviously, we know that  $J_{11}$ ,  $J_{22}$ ,  $J_{33}$ , ... etc. are zero and that  $J_{13} = J_{31}$ ,  $J_{12} = J_{21}$ , ..., etc. So from the output we can easily obtain the matrix element between any two basic state wavefunctions.

In order to handle larger spin systems, the input basic state wavefunctions of a system can be broken down into many subgroups, and each time we may take one subgroup as the input basic state wavefunctions. For example, in a five-spin system, there are a total of thirty-two basic state wavefunctions; each time we can take eight or sixteen basic state wavefunctions, as input. The size of the subgroup (the total number of basic state wavefunction of the subgroup) depends entirely on the size of the system (total number of nuclei) and the capacity of the computer. One can also use the basic state functions with the same projection of spin angular momentum  $M_s$  whichever is more convenient for the computer.

This program has proved to be very useful for the detailed analysis of high-resolution NMR spectra of larger spin systems [4] especially in using Whitman's [5], [6] direct-analysis NMR-spectra method or many other methods [7].

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