More on Magnetic Resonance*

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1 Splitting Spin States

1.1 Single Spin 1/2 Particle Splitting

In the presence of a magnetic field, the energies of the two spin states split, one being a higher energy and the other being a lower energy. Technically,

$$H_{op} = -\mu_z \cdot H_z$$

where H_z is the z-component (usually the sole component, since this defines the z-axis) of the magnetic field. We are assuming the magnetic dipole, $\vec{\mu}$ is proportional to the spin ($\vec{S}\ or\ \vec{I}$) i.e.,

$$\vec{\mu} = \kappa\hbar\vec{I} = \kappa\vec{S}$$

where κ is a constant. Then one would have

$$H_{op} = -\frac{\gamma}{2}\vec{S} \cdot H_z = -\frac{\gamma}{2}S_z H_z = -\frac{\gamma}{2}S_z H_z$$

1.2 Two Spin 1/2 Particle Splitting

When there are more than one spin, each may be in a different magnetic environment, so, for a two spin system, one might have

$$H_{op} = -\vec{\mu_1} \cdot \left((1-\sigma_1)\vec{B}\right) - \vec{\mu_2} \cdot \left((1-\sigma_2)\vec{B}\right)$$

*l2h2:loop2.tex

where σ is the nuclear magnetic shielding which, coupled with $\vec{B}$, defines a local magnetic field which might be different from the gross, macro one. This assumes that the two spins do not interact with each other.

When they do, this equation must be modified:

$$H_{op} = -(1-\sigma_1)\vec{\mu_1} \cdot \vec{B} - (1-\sigma_2)\vec{\mu_2} \cdot \vec{B} - J\vec{\mu_1} \cdot \vec{\mu_2} \tag{1}$$

since each magnetic moment (spin) creates a field which the other sees (and interacts with). Appropriately, this term is associated with spin-spin coupling!

2 Operator Representation of Spin

The basis for dealing with spin is a spin up or a spin down representation, and there are various flavors for doing this. In first year chemistry we learn +1/2 and -1/2 as the quantum numbers associated with spin, and perhaps later was mentioned that the spin states are often written as α and β. We could just as easily write "up" and "down" for α and β.

In a matrix representation, the basis set become vectors, which are represented by things such as

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and

$$\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The Pauli Spin Matrices are (written for nuclei, using I, rather than for electrons, where tradition says, σ)

$$I_y \equiv \begin{pmatrix} 0 & \frac{1}{2\imath} \\ -\frac{1}{2\imath} & 0 \end{pmatrix} \tag{2}$$

which translates into

$$= I_y|\alpha >= -\frac{1}{2\imath}|\beta >$$
$$I_y|\beta >= \frac{1}{2\imath}|\alpha >$$

and

$$I_z \equiv \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \tag{3}$$

whose meaning is apparent, and finally

$$I_x \equiv \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \tag{4}$$

which means

$$I_x \equiv \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix} = I_x|\alpha >= \frac{1}{2}|\beta > \tag{5}$$

We note that

$$I_x^2 = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} \tag{6}$$

$$I_y^2 = \begin{pmatrix} 0 & \frac{1}{2\imath} \\ -\frac{1}{2\imath} & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & \frac{1}{2\imath} \\ -\frac{1}{2\imath} & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \tag{7}$$

$$I_z^2 = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \otimes \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} \tag{8}$$

so, the sum of these three is

$$I_x^2 + I_y^2 + I_z^2 = I^2 = \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix} \tag{9}$$

Note that I^2 and I_z are simultaneously diagonal, something which is meaningful in quantum mechanics (they are simultaneously measureable).

Next, we form the Ladder Operators I_+ and I_- These are defined in analogy with angular momentum as

$$I_+ = I_x + \imath I_y$$

and

$$I_- = I_x - \imath I_y$$

$$I_+ \equiv \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} + \imath \begin{pmatrix} 0 & \frac{1}{2\imath} \\ -\frac{1\imath}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{2} + \imath\frac{1}{2\imath} \\ \frac{1}{2} - \imath\frac{1}{2\imath} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$I_- \equiv \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} - \imath \begin{pmatrix} 0 & \frac{1}{2\imath} \\ -\frac{1\imath}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{2} - \imath\frac{1}{2\imath} \\ \frac{1}{2} + \imath\frac{1}{2\imath} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

It is a simple matter to show that these matrices correctly emulate the expected ladder behavior, i.e., $I_+|\beta >= 1|\alpha >$ and $I_-|\alpha >= 1|\beta >$.

2.1 Matrix Representation of Two Spin Hamiltonian

We seek the four dimensional representation for two-spin systems.

What is the matrix representation of H_{op}? We start with the basis set, which consists of 4 functions, $|\alpha, \alpha >$, $|\alpha, \beta >$, $|\beta, \alpha >$, and $|\beta, \beta >$, where the first position refers to spin 1 and the second refers to spin 2. We have

$$\alpha(1)\alpha(2) \equiv |\alpha, \alpha >= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\alpha(1)\beta(2) \equiv |\alpha, \beta >= \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\beta(1)\alpha(2) \equiv |\beta, \alpha >= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$\beta(1)\beta(2) \equiv |\beta, \beta >= \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

and we need representations of the overall spin's components to allow us to create the matrix representation of the Hamiltonian. Such representations would correspond to a matrix formulation based on the labelling shown:

$$I_{whatever} = \begin{array}{cc} & \begin{array}{cccc} \alpha,\alpha & \alpha,\beta & \beta,\alpha & \beta,\beta \end{array} \\ \begin{array}{c} \alpha,\alpha \\ \alpha,\beta \\ \beta,\alpha \\ \beta\beta \end{array} & \begin{pmatrix} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix} \end{array} \tag{10}$$

2.1.1 The I_z Matrix Elements

We start with I_z. We know that the matrix form of I_z has got to look something like

$$I_z \mapsto \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{11}$$

indicating that when the two spins are opposed, the total z-component of spin of the composite, is zero, while when the two spins are parallel, either "up" or "down", then the z-components "add" or "subtract". Analytically, one has

$$(I_{z_1} + I_{z_2})\,|\alpha,\alpha >= I_{z_1}|\alpha,\alpha > + I_{z_2}|\alpha,\alpha >$$

which is

$$I_{z_1}|\alpha,\alpha > + I_{z_2}|\alpha,\alpha >= \frac{1}{2}|\alpha,\alpha > + \frac{1}{2}|\alpha,\alpha > \mapsto 1|\alpha,\alpha >$$

where, remember, $|one, two >$ represents the spin state of spin 1 (left) and spin 2 (right), which here are both "up". This is where the 1,1 element in Equation 11 comes from. To see this (and how all the matrix elements {i,1} are obtained), we left "multiply" by

$$\begin{matrix} < \alpha,\alpha| \\ < \alpha,\beta| \\ < \beta,\alpha| \\ < \beta,\beta| \end{matrix} \; (I_{z_1}|\alpha,\alpha > + I_{z_2}|\alpha,\alpha >) \mapsto \left(\frac{1}{2} + \frac{1}{2}\right) \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

since the "dot" products all vanish unless both "indices" are identical.

2.1.2 The I_x Matrix Elements

Next we look at the x-component of spin. We have

$$(I_{x_1} + I_{x_2})|\alpha,\alpha >= I_{x_1}|\alpha,\alpha > + I_{x_2}|\alpha,\alpha >= \frac{1}{2}|\beta,\alpha > + \frac{1}{2}|\alpha,\beta >$$

Left multiplying (as before, we have

$$\begin{pmatrix} < \alpha,\alpha| \\ < \alpha,\beta| \\ < \beta,\alpha| \\ < \beta,\beta| \end{pmatrix} (I_{x_1} + I_{x_2})|\alpha,\alpha >) \mapsto \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$$

Therefore, we know

$$I_x|\alpha,\alpha>=\begin{pmatrix} 0 & ? & ? & ? \\ \frac{1}{2} & ? & ? & ? \\ \frac{1}{2} & ? & ? & ? \\ 0 & ? & ? & ? \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}=\frac{1}{2}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \tag{12}$$

$$(I_{x_1}+I_{x_2})|\alpha,\beta>=I_{x_1}|\alpha,\beta>+I_{x_2}|\alpha,\beta>=\frac{1}{2}|\beta,\beta>+\frac{1}{2}|\alpha,\alpha>$$

$$\begin{matrix} <\alpha,\alpha| \\ <\alpha,\beta| \\ <\beta,\alpha| \\ <\beta,\beta| \end{matrix}(I_{x_1}+I_{x_2})|\alpha,\beta>)\mapsto\frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

so

$$\begin{pmatrix} 0 & \frac{1}{2} & ? & ? \\ \frac{1}{2} & 0 & ? & ? \\ \frac{1}{2} & 0 & ? & ? \\ 0 & \frac{1}{2} & ? & ? \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}=\frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{13}$$

$$(I_{x_1}+I_{x_2})|\beta,\alpha>=I_{x_1}|\beta,\alpha>+I_{x_2}|\beta,\alpha>=\frac{1}{2}|\alpha,\alpha>+\frac{1}{2}|\beta,\beta>$$

$$\begin{matrix} <\alpha,\alpha| \\ <\alpha,\beta| \\ <\beta,\alpha| \\ <\beta,\beta| \end{matrix}(I_{x_1}+I_{x_2})|\beta,\alpha>)\mapsto\frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

so

$$\begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & ? \\ \frac{1}{2} & 0 & 0 & ? \\ \frac{1}{2} & 0 & 0 & ? \\ 0 & \frac{1}{2} & \frac{1}{2} & ? \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}=\frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{14}$$

$$(I_{x_1}+I_{x_2})|\beta,\beta>=I_{x_1}|\beta,\beta>+I_{x_2}|\beta,\beta>=\frac{1}{2}|\alpha,\beta>+\frac{1}{2}|\beta,\alpha>$$

$$\begin{matrix} <\alpha,\alpha| \\ <\alpha,\beta| \\ <\beta,\alpha| \\ <\beta,\beta| \end{matrix}(I_{x_1}+I_{x_2})|\alpha,\alpha>)\mapsto\frac{1}{2}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$$

and finally,

$$I_{x_1} + I_{x_2} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \tag{15}$$

and

$$\begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \tag{16}$$

Parenthetically, we calculate the square of this matrix quickly, i.e.,

$$I_x^2 = (I_{x_1} + I_{x_2})^2 = \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix} \tag{17}$$

2.1.3 The I_y Matrix Elements

For I_y we have

$$(I_{y_1} + I_{y_2})|\alpha, \alpha >= I_{y_1}|\alpha, \alpha > + I_{y_2}|\alpha, \alpha >= -\frac{1}{2\imath}|\beta, \alpha > -\frac{1}{2\imath}|\alpha, \beta >$$

Therefore, we know

$$I_y = \begin{pmatrix} 0 & ? & ? & ? \\ -\frac{1}{2\imath} & ? & ? & ? \\ -\frac{1}{2\imath} & ? & ? & ? \\ 0 & ? & ? & ? \end{pmatrix} \tag{18}$$

$$(I_{y_1} + I_{y_2})|\alpha, \beta >= I_{y_1}|\alpha, \beta > + I_{y_2}|\alpha, \beta >= -\frac{1}{2}|\beta, \beta > +\frac{1}{2}|\alpha, \alpha >$$

so

$$\begin{pmatrix} 0 & \frac{1}{2\imath} & ? & ? \\ -\frac{1}{2\imath} & 0 & ? & ? \\ -\frac{1}{2\imath} & 0 & ? & ? \\ 0 & \frac{-1}{2\imath} & ? & ? \end{pmatrix} \tag{19}$$

$$(I_{y_1}+I_{y_2})|\beta,\alpha>=I_{y_1}|\beta,\alpha>+I_{y_2}|\beta,\alpha>=\frac{1}{2}|\alpha,\alpha>-\frac{1}{2}|\beta,\beta>$$

so

$$\begin{pmatrix} 0 & \frac{1}{2\imath} & \frac{1}{2\imath} & ? \\ -\frac{1}{2\imath} & 0 & 0 & ? \\ -\frac{1}{2\imath} & 0 & 0 & ? \\ 0 & -\frac{1}{2\imath} & -\frac{1}{2\imath} & ? \end{pmatrix} \tag{20}$$

$$(I_{y_1}+I_{y_2})|\beta,\beta>=I_{y_1}|\beta,\beta>+I_{y_2}|\beta,\beta>=+\frac{1}{2}|\alpha,\beta>+\frac{1}{2}|\beta,\alpha>$$

so

$$I_y=\begin{pmatrix} 0 & \frac{1}{2\imath} & \frac{1}{2\imath} & 0 \\ -\frac{1}{2\imath} & 0 & 0 & +\frac{1}{2\imath} \\ -\frac{1}{2\imath} & 0 & 0 & +\frac{1}{2\imath} \\ 0 & -\frac{1}{2\imath} & -\frac{1}{2\imath} & 0 \end{pmatrix}=\frac{1}{2\imath}\begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix} \tag{21}$$

Again, we calculate (as we did in Equation 16 the square of this matrix (as we did before, see Equation 16) quickly, i.e.,

$$(I_{y_1}+I_{y_2})^2=\left(\frac{1}{2\imath}\right)^2\begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix}\otimes\begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix}$$

$$=-\frac{1}{2}\begin{pmatrix} -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \\ 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix}=\frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix} \tag{22}$$

And we're done!

Well, not quite. Let's verify that the overall spin is correctly accounted for (using I_z, in Equation 11), using Equation 11 as well as Equations 16 and 22 i.e.,

$$I_x^2+I_y^2+I_z^2=\frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix}\oplus\frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix}\oplus 1\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$=1\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \tag{23}$$

This is not quite what we hoped for. We wanted a diagonal matrix, which, when coupled with the I_z matrix which we know is diagonal, would allow us to state that it was possible to simulatenously measure I_z and I^2 in this two spin system. The complication is the central square in the I^2 matrix. We know, from tons of earlier work, that there exists a set of eigenvectors of the I^2 operator (matrix) which form a representation in which the I^2 and I_z matrices are diagaonal. They are

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \; and \; \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \; and \; \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \; and \; \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{24}$$

which gives diagonal (eigenvalues) for I^2 of 2, 2, 2, and zero. We have rederived the well known fact that the two spin system devolves down to a triplet and a singlet state.

To see this, we form the abutted matrix of concatenated eigenvectors (in normalized form)

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = T_{eig} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix} \tag{25}$$

so, in normalized form:

$$T_{eig} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \; ; \; T_{eig}^{transpose} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{26}$$

and

$$T_{eig}^{transpose} \otimes I^2 \otimes T_{eig} = 1 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{27}$$

$$= 1 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & \frac{2}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{2}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \tag{28}$$

and finally

$$= 1 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \tag{29}$$

which gives diagonal (eigenvalues) for I^2 of 2, 2, 2, and zero. Notice that the eigenvectors which are symmetric are associated with the eigenvalue 2, while the antisymmetric eigenfunction is associated with the eigenvalue 0. Remember that s(s+1) becomes something like i(i+1) which yields the value of 2 (above).

2.1.4 I_z in this Representation

We wish to check the form for I_z in this repesentation, i.e.,

$$T_{eig}^{transpose} \otimes I_z \otimes T_{eig} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{30}$$

2.2 Interpretation using Ladder Operators

We now employ the ladder operators

$$I_+ = I_x + iI_y$$

and

$$I_- = I_x - iI_y$$

We obtain their matrix representations:

$$I^{+} = I_x + \imath I_y = \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} + \imath \frac{1}{2\imath}\begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix} = 1\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{31}$$

$$I^{-} = I_x - \imath I_y = \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} - \imath \frac{1}{2\imath}\begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix} = 1\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix} \tag{32}$$

2.2.1 Verifying the Operation of Ladder Operators

We can verify Equations 31 and 32 thus:

$$I^{+}|\alpha,\alpha >= 1\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = I^{+}|\alpha,\alpha >= 0$$

$$I^{+}|\alpha,\beta >= 1\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 1\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 1|\alpha,\alpha >$$

$$I^{+}|\beta,\alpha >= 1\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = 1\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 1|\alpha,\alpha >$$

$$I^{+}|\beta,\beta >= 1\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} = 1\left(|\alpha,\beta > + |\beta,\alpha >\right)$$

For I^- we have

$$I^-|\alpha,\alpha>= 1\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} = 1\,(|\alpha,\beta> + |\beta,\alpha>)$$

$$I^-|\alpha,\beta>= 1\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 1|\beta,\beta>$$

$$I^-|\beta,\alpha>= 1\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 1|\beta,\beta>$$

$$I^-|\beta,\beta>= 1\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 0$$

2.3 Returning to the Main Hamiltonian Problem

Since the chemical shifts are assumed different, i.e., $(\sigma_1 \neq \sigma_2)$, we need to be very careful in separating the effects on spin 1 and spin 2.

2.3.1 The I_{x_n} Matrix Elements

In order to interpret the Hamiltonian's dot product $\vec{I_1}\cdot\vec{I_2}$, we need to represent the individual spin operators properly.

Since we already used

$$(I_{x_1} + I_{x_2})|\alpha,\alpha>= I_{x_1}|\alpha,\alpha> + I_{x_2}|\alpha,\alpha>= \frac{1}{2}|\beta,\alpha> + \frac{1}{2}|\alpha,\beta>$$

we can now form $<\alpha,\alpha|(I_{x_1})|\alpha,\alpha>$ to obtain the matrix representation of I_{x_1}. We would have

$$<\beta,\alpha|(I_{x_1})|\alpha,\alpha>=<\beta,\alpha|\frac{1}{2}|\beta,\alpha>= \frac{1}{2}$$

$$
\begin{aligned}
< \beta,\beta|(I_{x_1})|\alpha,\beta >=< \beta,\beta|\frac{1}{2}|\beta,\beta >= \frac{1}{2} \\
< \alpha,\alpha|(I_{x_1})|\beta,\alpha >=< \alpha,\alpha|\frac{1}{2}|\alpha,\alpha >= \frac{1}{2} \\
< \alpha,\beta|(I_{x_1})|\beta,\beta >=< \alpha,\beta|\frac{1}{2}|\alpha,\beta >= \frac{1}{2}
\end{aligned} \tag{33}
$$

and

$$
\begin{aligned}
< \alpha,\beta|(I_{x_2})|\alpha,\alpha >=< \alpha,\beta|\frac{1}{2}|\alpha,\beta >= \frac{1}{2} \\
< \alpha,\alpha|(I_{x_2})|\alpha,\beta >=< \alpha,\alpha|\frac{1}{2}|\alpha,\alpha >= \frac{1}{2} \\
< \beta,\beta|(I_{x_2})|\beta,\alpha >=< \beta,\beta|\frac{1}{2}|\beta,\beta >= \frac{1}{2} \\
< \beta,\alpha|(I_{x_2})|\beta,\beta >=< \beta,\alpha|\frac{1}{2\imath}|\beta,\alpha >= \frac{1}{2}
\end{aligned} \tag{34}
$$

Therefore, we have

$$
I_{x_1} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{35}
$$

and

$$
I_{x_2} = \frac{1}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{36}
$$

in the two-spin basis set.

One sees that if one adds these two together, one obtains Equation 15.

2.3.2 The I_{y_n} Matrix Elements

We can now form $< \alpha,\alpha|(I_{y_1})|\alpha,\alpha >$ etc., to obtain the matrix representation of I_{y_1}. We would have:

$$
\begin{aligned}
< \beta,\alpha|(I_{y_1})|\alpha,\alpha >=< \beta,\alpha|\frac{-1}{2\imath}|\beta,\alpha >= -\frac{1}{2\imath} \\
< \beta,\beta|(I_{y_1})|\alpha,\beta >=< \beta,\beta|\frac{-1}{2\imath}|\beta,\beta >= -\frac{1}{2\imath}
\end{aligned}
$$

$$
\begin{aligned}
< \alpha,\alpha|(I_{y_1})|\beta,\alpha > &= < \alpha,\alpha|\frac{1}{2\imath}|\alpha,\alpha > = \frac{1}{2\imath} \\
< \alpha,\beta|(I_{y_1})|\beta,\beta > &= < \alpha,\beta|\frac{1}{2\imath}|\alpha,\beta > = \frac{1}{2\imath}
\end{aligned}
\tag{37}
$$

Therefore, we have

$$
I_{y_1} = \frac{1}{2\imath}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}
\tag{38}
$$

in the two-spin basis set. For the other spin, one would have

$$
\begin{aligned}
< \alpha,\beta|(I_{y_2})|\alpha,\alpha > &= < \alpha,\beta|\frac{-1}{2\imath}|\alpha,\beta > = -\frac{1}{2\imath} \\
< \alpha,\alpha|(I_{y_2})|\alpha,\beta > &= < \alpha,\alpha|\frac{1}{2\imath}|\alpha,\alpha > = \frac{1}{2\imath} \\
< \beta,\beta|(I_{y_2})|\beta,\alpha > &= < \beta,\beta|\frac{-1}{2\imath}|\beta,\beta > = -\frac{1}{2\imath} \\
< \beta,\alpha|(I_{y_2})|\beta,\beta > &= < \beta,\alpha|\frac{1}{2}|\beta,\alpha > = \frac{1}{2}
\end{aligned}
\tag{39}
$$

i.e.,

$$
I_{y_2} = \frac{1}{2\imath}\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}
\tag{40}
$$

These last two matrices, when added together, should give Equation 21.

2.4 The I_{z_n} Matrix Elements

Last, and least, we need the diagonal elements of I_z. We have

$$
\begin{aligned}
< \alpha,\alpha|(I_{z_1})|\alpha,\alpha > &= < \alpha,\alpha|\frac{1}{2}|\alpha,\alpha > = \frac{1}{2} \\
< \alpha,\beta|(I_{z_1})|\alpha,\beta > &= < \alpha,\beta| - \frac{1}{2}|\alpha,\beta > = -\frac{1}{2} \\
< \beta,\alpha|(I_{z_1})|\beta,\alpha > &= < \beta,\alpha|\frac{1}{2}|\beta,\alpha > = \frac{1}{2}
\end{aligned}
$$

$$
\begin{aligned}
< \beta,\beta|(I_{z_1})|\beta,\beta >=< \beta,\beta| -\frac{1}{2}|\beta,\beta >= -\frac{1}{2} \\
< \alpha,\alpha|(I_{z_2})|\alpha,\alpha >=< \alpha,\alpha|\frac{1}{2}|\alpha,\alpha >= \frac{1}{2} \\
< \alpha,\beta|(I_{z_2})|\alpha,\beta >=< \alpha,\beta|\frac{1}{2}|\alpha,\beta >= \frac{1}{2} \\
< \beta,\alpha|(I_{z_2})|\beta,\alpha >=< \beta,\alpha| -\frac{1}{2}|\beta,\alpha >= -\frac{1}{2} \\
< \beta,\beta|(I_{z_2})|\beta,\beta >=< \beta,\beta| -\frac{1}{2}|\beta,\beta >= -\frac{1}{2}
\end{aligned} \tag{41}
$$

so

$$
I_{z_1} = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{42}
$$

and

$$
I_{z_2} = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{43}
$$

2.5 The Hamiltonian

Having "looked" at I_z and the various other spin operators in this new four-dimensional world, we now turn to H_{op} and attempt to generate (see Equation 1) the 4x4 matrix representation of this operator. We have, for the $|\alpha,\alpha >$ state:

$$
H_{op}|\alpha,\alpha >= \left(-\frac{\gamma}{2}(1-\sigma_1)I_{z_1}H_z - \frac{\gamma}{2}(1-\sigma_2)I_{z_2}H_z - J\vec{I_1}\cdot\vec{I_2}\right)|\alpha,\alpha >
$$

which is

$$
= -\frac{\gamma}{2}(1-\sigma_1)\frac{1}{2}H_z|\alpha,\alpha > -\frac{\gamma}{2}(1-\sigma_2)\frac{1}{2}H_z|\alpha,\alpha > -J\vec{I_1}\cdot\vec{I_2}|\alpha,\alpha >
$$

The last term expands to

$$
-J\left(I_{x_1}I_{x_2}|\alpha,\alpha > +I_{y_1}I_{y_2}|\alpha,\alpha > +I_{z_1}I_{z_2}|\alpha,\alpha >\right) \tag{44}
$$

2.6 The Spin-Spin Coupling Term

We will need

$$I_{x_1} \cdot I_{x_2} = \frac{1}{4} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \tag{45}$$

and

$$\begin{aligned} I_{y_1} \cdot I_{y_2} &= -\frac{1}{4} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} = -\frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \\ &= \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \end{aligned} \tag{46}$$

$$I_{z_1} \cdot I_{z_2} = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{47}$$

$$I_{x_1} \cdot I_{x_2} + I_{y_1} \cdot I_{y_2} + I_{z_1} \cdot I_{z_2} = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \oplus \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \oplus \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{48}$$

which is

$$I_{x_1} \cdot I_{x_2} + I_{y_1} \cdot I_{y_2} + I_{z_1} \cdot I_{z_2} = \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4}1 \end{pmatrix} \tag{49}$$

This last form will be just right for combining with the chemical shift term to form the entire Hamiltonian.

2.7 Returning to the Main Hamiltonian Problem using Ladder Operators

So, solving for I_x one has

$$I_x = \frac{I_+ + I_-}{2}$$

and for I_y one has

$$I_y = \frac{I_+ - I_-}{2\imath}$$

One verifies that the latter two equations are properly represented by the two matrix forms of I_+ and I_- (above).

Returning now to evaluating the last term in equation 44

$$-J\left(I_{x_1}\cdot I_{x_2} + I_{y_1}\cdot I_{y_2} + I_{z_1}\cdot I_{z_2}\right)|\alpha,\alpha>=$$

$$\frac{J}{4}\left((I_{+_1}+I_{-_1})(I_{+_2}+I_{-_2}) - (I_{+_1}-I_{-_1})(I_{+_2}-I_{-_2})\right)|\alpha,\alpha> + JI_{z_1}I_{z_2}|\alpha,\alpha>$$

$$\begin{aligned}
&= \frac{J}{4}\left(I_{+_1}(I_{+_2} + I_{+_1}I_{-_2} + I_{-_1}I_{+_2} + I_{-_1}I_{-_2}\right)|\alpha,\alpha> \\
&\quad -\frac{J}{4}\left(I_{+_1}I_{+_2} - I_{+_1}I_{-_2}) - I_{-_1}I_{+_2}I_{-_1}I_{-_2}\right)|\alpha,\alpha> \\
&\quad + JI_{z_1}I_{z_2}|\alpha,\alpha>
\end{aligned}$$

Remember that $I_+|\alpha>=0$ and *vice versa* for the down operator, leading to

$$-J\left(I_1\cdot I_2\right)|\alpha,\alpha>= -J\frac{1}{4}\left(1|\beta,\beta> -1|\beta,\beta> +1|\alpha,\alpha>\right)$$

$$-J\left(I_1\cdot I_2\right)|\alpha,\alpha>= -J\frac{1}{4}1|\alpha,\alpha>$$

2.7.1 The Elements Related to $|\alpha,\alpha>$

The matrix elements are then

$$<\alpha,\alpha|H_{op}|\alpha,\alpha>= \left(-\frac{\gamma}{2}(1-\sigma_1) - \frac{\gamma}{2}(1-\sigma_2)\right)\frac{1H_z}{2} - J\frac{1}{4} \tag{50}$$

$$<\alpha,\beta|H_{op}|\alpha,\alpha>= 0 \tag{51}$$

$$<\beta,\beta|H_{op}|\alpha,\alpha>= 0 \tag{52}$$

$$<\beta,\alpha|H_{op}|\alpha,\alpha>= 0 \tag{53}$$

2.7.2 The Elements Related to $|\alpha, \beta>$

Now we repeat the job based on $|\alpha, \beta>$. We have

$$H_{op}|\alpha, \beta >= \left(-\frac{\gamma}{2}(1-\sigma_1)I_{z_1}H_z - \frac{\gamma}{2}(1-\sigma_2)I_{z_2}H_z - J\vec{I_1}\cdot\vec{I_2}\right)|\alpha, \beta >$$

$$H_{op}|\alpha, \beta >= \left(-\frac{\gamma}{2}(1-\sigma_1)H_z\left(\frac{1}{2}\right) - \frac{\gamma}{2}(1-\sigma_2)H_z\left(\frac{-1}{2}\right) - J\vec{I_1}\cdot\vec{I_2}\right)|\alpha, \beta >$$

so all we need to do is look at the spin-spin coupling term (J).

$$-J\left(I_{x_1}\cdot I_{x_2} + I_{y_1}\cdot I_{y_2} + I_{z_1}\cdot I_{z_2}\right)|\alpha, \beta >=$$
$$-J\frac{1}{4}\left((I_{+_1}+I_{-_1})(I_{+_2}+I_{-_2}) + (I_{+_1}-I_{-_1})(I_{+_2}-I_{-_2})|\alpha, \beta > + I_{z_1}I_{z_2}|\alpha, \beta >\right) =$$
$$-\frac{J}{4}\left(I_{+_1}I_{+2} + I_{+1}I_{-2} + I_{-1}I_{+2} + I_{-1}I_{-2} + \left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\right)|\alpha, \beta >$$

and resolving the ladder up and down operators one has

$$\begin{aligned}
(I_{+_1}+I_{+_2})|\alpha, \beta > &= 0\\
(I_{+_1}+I_{-_2})|\alpha, \beta > &= 0\\
(I_{-_1}+I_{+_2})|\alpha, \beta > &= 1|\beta, \alpha >\\
(I_{-_1}+I_{-_2})|\alpha, \beta > &= 0
\end{aligned}$$

i.e.,

$$-\frac{J}{4}\left(I_{+_1}I_{+2} + I_{+1}I_{-2} + I_{-1}I_{+2} + I_{-1}I_{-2} + \left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\right)|\alpha, \beta >= -\frac{J}{4}\left(1|\beta, \alpha > -1|\alpha, \beta >\right) \tag{54}$$

Ah.

From these, we obtain the appropriate matrix elements

$$H_{op}|\alpha, \beta >= \left(-\frac{\gamma}{2}(1-\sigma_1)H_z\left(\frac{1}{2}\right) - \frac{\gamma}{2}(1-\sigma_2)H_z\left(\frac{-1}{2}\right)\right)|\alpha, \beta > -\frac{J}{4}\left(1|\beta, \alpha > -1|\alpha, \beta >\right) \tag{55}$$

$$< \alpha, \beta|H_{op}|\alpha, \beta >= \left(-\frac{\gamma}{2}(1-\sigma_1) - \frac{\gamma}{2}(1-\sigma_2)\right)\frac{1H_z}{2} + J\frac{1}{4}$$

$$< \alpha, \alpha|H_{op}|\alpha, \beta >= 0$$

$$< \beta, \beta | H_{op} | \alpha, \beta >= 0$$

$$< \beta, \alpha | H_{op} | \alpha, \beta >= -J\frac{1}{4}$$

Next, we repeat the job based on $|\beta, \alpha >$. We have

$$H_{op}|\beta, \alpha >= \left(-\frac{\gamma}{2}(1-\sigma_1)I_{z_1}H_z - \frac{\gamma}{2}(1-\sigma_2)I_{z_2}H_z - J\vec{I_1}\cdot\vec{I_2} \right) |\beta, \alpha >$$

so

$$< \beta, \alpha | H_{op} | \alpha, \beta >= \left(-\frac{\gamma}{2}(1-\sigma_1) + \frac{\gamma}{2}(1-\sigma_2) \right) \frac{H_z}{2} - \frac{J}{4} \quad (56)$$

$$< \alpha, \beta | H_{op} | \alpha, \beta >= +\frac{J}{4} \quad (57)$$

$$< \alpha, \alpha | H_{op} | \alpha, \beta >= 0 \quad (58)$$

$$< \beta, \beta | H_{op} | \alpha, \beta >= 0 \quad (59)$$

3 Revisting Spin-Spin Coupling Using an Alternative Method

Consider a molecule with two different protons which interact. The Hamiltonian for the system will be

$$H = -\frac{\gamma}{2}\left((1-\sigma_1)\vec{B_0}\cdot\vec{I_1} + (1-\sigma_2)\vec{B_0}\cdot\vec{I_2} \right) - J(\vec{I_1}\cdot\vec{I_2})$$

Here, σ_1 and σ_2 when different, indicate that the two protons have different chemically shifted environments, a so-called AB system, where if $\sigma_1 = \sigma_2$ then we have an A_2 system. The last term, $J(\vec{I_1}\cdot\vec{I_2})$ is the spin-spin coupling term. γ is the gyromagnetic ratio, and the term $\vec{B_0}\cdot\vec{I}$ is usually set up so that the z-component of $\vec{B}$ is multiplied onto the z-component of the spin, $\hat{k}\cdot\vec{I} \rightarrow I_z$, so that we have

$$H = -\frac{\gamma}{2}(2-\sigma_1-\sigma_2)\vec{B}_{z_0}\cdot(\vec{I}_{z_1}+\vec{I}_{z_2}) - J(\vec{I_1}\cdot\vec{I_2})$$

Now we need to work out the matrix representative of this Hamiltonian, diagonalize it, and see what happens in the case $J = 0$ and $J > 0$, as well as $\sigma_1 = \sigma_2$ and $\sigma_1 \neq \sigma_2$.

4 The dot product

$$\vec{I}_1 \cdot \vec{I}_2 = I_{x_1} \cdot I_{x_2} + I_{y_1} \cdot I_{y_2} + I_{z_1} \cdot I_{z_2} \tag{60}$$

by definition so knowing that

$$\begin{aligned} I_{+_1} &= I_{x_1} + \imath I_{y_1} \\ I_{-_1} &= I_{x_1} - \imath I_{y_1} \\ I_{+_2} &= I_{x_2} + \imath I_{y_2} \\ I_{-_2} &= I_{x_2} - \imath I_{y_2} \end{aligned}$$

it follows that

$$\begin{aligned} I_{x_1} &= \frac{1}{2}\left(I_{+_1} + I_{-_1}\right) \\ I_{y_1} &= \frac{1}{2\imath}\left(I_{+_1} - I_{-_1}\right) \\ I_{x_2} &= \frac{1}{2}\left(I_{+_2} + I_{-_2}\right) \\ I_{y_2} &= \frac{1}{2\imath}\left(I_{+_2} - I_{-_2}\right) \end{aligned}$$

so, substituting into Equation 60 we have

$$\vec{I}_1 \cdot \vec{I}_2 = \frac{1}{2}\left(I_{+_1} + I_{-_1}\right) \cdot \frac{1}{2}\left(I_{+_2} + I_{-_2}\right) + \frac{1}{2\imath}\left(I_{+_1} - I_{-_1}\right) \cdot \frac{1}{2\imath}\left(I_{+_2} - I_{-_2}\right) + I_{z_1} \cdot I_{z_2}$$

Now for a two spin system, we are going to use the basis vectors

$$|\alpha, \alpha >= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$|\beta, \alpha >= \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$|\alpha, \beta >= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

and

$$|\beta,\beta> \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

all we need do is to investigate how the dot product operator (and the rest of the Hamiltonian) is going to operate on these, to obtain a matrix representation of the Hamiltonian operator in this basis set. The last term of the dot product part of the Hamiltonian is trivial, i.e.,

$$I_{z_1} \cdot I_{z_2}|\alpha,\alpha>= \frac{1}{4}|\alpha,\alpha>$$

(where $\frac{1}{4} = \left(\frac{1}{2}\right)^2$). Then we have

$$I_{z_1} \cdot I_{z_2}|\beta,\alpha>= -\frac{1}{4}|\beta,\alpha>$$

$$I_{z_1} \cdot I_{z_2}|\alpha,\beta>= -\frac{1}{4}|\alpha,\beta>$$

and

$$I_{z_1} \cdot I_{z_2}|\beta,\beta>= \frac{1}{4}|\beta,\beta>$$

In order to obtain matrix elements, these results are "dotted" (from the left) by basis vectors such as $<\alpha,\beta|$, which then uses the $<|$ and $|>$ contents as indices in the matrix formulation. So, the matrix representative of this part of the Hamiltonian, absent the coupling constant, is

$$I_{z_1} \cdot I_{z_2} \equiv \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

5 Ladder Operators for $\vec{I}_1 \cdot \vec{I}_2$

It is the use of the ladder operators which requires some finesse. The residual part of $\vec{I}_1 \cdot \vec{I}_2$ which requires use of these ladder operators is:

$$\frac{1}{4}\left(I_{+_1} + I_{-_1}\right) \cdot \left(I_{+_2} + I_{-_2}\right) - \frac{1}{4}\left(I_{+_1} - I_{-_1}\right) \cdot \left(I_{+_2} - I_{-_2}\right)$$

and we will attempt operating with this operator on $|\alpha,\alpha>$ i.e.,

$$\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)\cdot\left(I_{+_2}+I_{-_2}\right)|\alpha,\alpha>\rightarrow\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)\cdot\left(|\alpha,\beta>\right)\rightarrow\frac{1}{4}\left(|\beta,\beta>\right)$$
$$-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)\cdot\left(-|\alpha,\beta>\right)\rightarrow-\frac{1}{4}\left(-\left(-|\beta,\beta>\right)\right)=-\frac{1}{4}|\beta,\beta> \quad (61)$$

Therefore

$$I_{x_1}\cdot I_{x_2}+I_{y_1}\cdot I_{y_2}\equiv\begin{pmatrix}0&?&?&?\\0&?&?&?\\0&?&?&?\\0&?&?&?\end{pmatrix}$$

which is certainly an exciting result.

$$\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)\cdot\left(I_{+_2}+I_{-_2}\right)|\alpha,\beta>\rightarrow\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)|\alpha,\alpha>\rightarrow\frac{1}{4}|\beta,\alpha>$$
$$-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)\cdot\left(I_{+_2}-I_{-_2}\right)|\alpha,\beta>\rightarrow-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)|\alpha,\alpha>\rightarrow-\frac{1}{4}\left(-|\beta,\alpha>\right) \quad (62)$$

Therefore

$$I_{x_1}\cdot I_{x_2}+I_{y_1}\cdot I_{y_2}\equiv\begin{pmatrix}0&0&?&?\\0&0&?&?\\0&\frac{1}{2}&?&?\\0&0&?&?\end{pmatrix}$$

Continuing, we have

$$\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)\cdot\left(I_{+_2}+I_{-_2}\right)|\beta,\alpha>\rightarrow\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)|\beta,\beta>\rightarrow\frac{1}{4}|\alpha,\beta>$$
$$-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)\cdot\left(I_{+_2}-I_{-_2}\right)|\beta,\alpha>\rightarrow-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)|\beta,\beta>\rightarrow-\frac{1}{4}\left(-|\alpha,\beta>\right) \quad (63)$$

Therefore

$$I_{x_1}\cdot I_{x_2}+I_{y_1}\cdot I_{y_2}\equiv\begin{pmatrix}0&0&0&?\\0&0&\frac{1}{2}&?\\0&\frac{1}{2}&0&?\\0&0&0&?\end{pmatrix}$$

$$\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)\cdot\left(I_{+_2}+I_{-_2}\right)|\beta,\beta>\rightarrow\frac{1}{4}\left(I_{+_1}+I_{-_1}\right)|\beta,\alpha>\rightarrow\frac{1}{4}|\alpha,\alpha>$$
$$-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)\cdot\left(I_{+_2}-I_{-_2}\right)|\beta,\beta>\rightarrow-\frac{1}{4}\left(I_{+_1}-I_{-_1}\right)|\beta,\alpha>\rightarrow-\frac{1}{4}\left(-|\alpha,\alpha>\right) \quad (64)$$

Therefore

$$I_{x_1} \cdot I_{x_2} + I_{y_1} \cdot I_{y_2} \equiv \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Therefore, the total dot product matrix representation becomes

$$\vec{I_1} \cdot \vec{I_2} = \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

and the Hamiltonian becomes, defining

$$H_{1,1} = -\gamma \left((1-\sigma_1)B_0 \frac{1}{2} + (1-\sigma_2)B_0 \frac{1}{2} \right) \tag{65}$$

$$H_{2,2} = -\gamma \left((1-\sigma_1)B_0 \frac{1}{2} - (1-\sigma_2)B_0 \frac{1}{2} \right) \tag{66}$$

$$H_{3,3} = -\gamma \left(-(1-\sigma_1)B_0 \frac{1}{2} + (1-\sigma_2)B_0 \frac{1}{2} \right) \tag{67}$$

$$H_{4,4} = -\gamma \left(-(1-\sigma_1)B_0 \frac{1}{2} - (1-\sigma_2)B_0 \frac{1}{2} \right) \tag{68}$$

we have

$$H = \begin{pmatrix} H_{1,1} - \frac{J}{4} & 0 & 0 & 0 \\ 0 & H_{2,2} + \frac{J}{4} & -\frac{J}{2} & 0 \\ 0 & -\frac{J}{2} & H_{3,3} + \frac{J}{4} & 0 \\ 0 & 0 & 0 & H_{4,4} - \frac{J}{4} \end{pmatrix} \tag{69}$$