Looking for a better way to do density matrix transformations PhL 1.7.08

Levitt makes it seem harder than I think it really is. He does not take a formal general view, but I am sure other books probably do. However, I don't have those other books. And this provides a good review.

This doc addresses not just this "general case" issue, but also some other things that have been bothering me. See also a separate Stern-Gerlach document. I think everything now makes sense.

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Precession for the AX System. Includes a picture to interpret a vector equation.

What does an x RF pulse do?
Causes precession of **I** within the rotating frame about the y-z axis!
Thus, a π/2 pulse rotates **I** down from z to -y.

Apply an RF pulse to a system at absolute zero temperature.
What happens to energy and to magnetization?

Point of Confusion-- RF radiation is very small so *much* longer than T_1 or T_2 to relax things

What is the meaning of an off-diagonal matrix element of the density matrix ρ ?
A. Opening Comments
B. Perturbation theory and Transition Rate

$$d\rho_{mn}(t)/dt = -\, i\, H'_{mn}\, \{\, \rho(t)_{nn} - \rho(t)_{mm} \,\}$$

Most General form of the Density Matrix for spin-1/2 and for spin-1/2 ⊗ spin-1/2.

The most general form of a tr(ρ) = 1 2x2 density matrix is this

$$\rho = 1/2 + \mathbf{a}\bullet\boldsymbol{\sigma}$$

[Start with $\rho = k_1 + \mathbf{k}_2\bullet\boldsymbol{\sigma}$ showing 4 parameters. Then tr(ρ)= 0 forces $k_1 = 1/2$.] Since ρ must be Hermitian, the three parameters **a** are real.

We can always express the 4x4 density matrix in this way [for uncoupled spins!]

$$\rho = \rho_1 \otimes \rho_2 = (1/2 + \mathbf{a_1}\bullet\boldsymbol{\sigma}) \otimes (1/2 + \mathbf{a_2}\bullet\boldsymbol{\sigma})$$

But it would be nice to have a better way to distinguish the two spaces so we can then eliminate the ⊗ symbol, which gets us closer to thinking of an actual 4x4 matrix. Suppose like Levitt we use x,y,z for the Cartesian labels, and use 1,2 to label the spaces. But suppose also we use **a** for the 1 space and **b** for the 2 space. Then we could say:

$$\rho = \rho_1 \otimes \rho_2 = (1/2 + \mathbf{a}\bullet\boldsymbol{\sigma}_1) \otimes (1/2 + \mathbf{b}\bullet\boldsymbol{\sigma}_2)$$

We might rescale this to **I** instead of **σ** to get closer to Levitt, so rescale this as

$$\rho = \rho_1 \otimes \rho_2 = (1/2 + \mathbf{a}\bullet\mathbf{I}_1) \otimes (1/2 + \mathbf{b}\bullet\mathbf{I}_2) \qquad \text{// final form}$$

We can then write this without the ⊗ sign as follows

$$\rho = 1/4 + 1/2\ [\ \mathbf{a}\bullet\mathbf{I}_1 + \mathbf{b}\bullet\mathbf{I}_2] + \mathbf{a}\bullet\mathbf{I}_1\,\mathbf{b}\bullet\mathbf{I}_2$$

where I think it is always clear "what we mean" by each term. We could expand the dot products either in the usual way, or in a way using + and − operators, but for now we think of either as possible. You can always think of the above ρ and I as either a matrix or a Hilbert Space operator.

Notice that the ρ shown above has only 6 real parameters. More generally, such as when the two spins are coupled as in the J-coupling, the number of parameters is this: 3 reals for the diagonal (trρ=1), then 6 complex numbers for the upper triangular matrix. So there are then 3 + 2*6 = 15 real parameters. We can express such a ρ in the following manner:

$$\rho = \Sigma_{\mu=0,3}\,\Sigma_{\upsilon=0,3}\ A_{\mu\upsilon}\ I_\mu \otimes I_\upsilon \quad = \Sigma_{\mu\upsilon}\ A_{\mu\upsilon}\ I_{1\mu} I_{2\upsilon} \qquad \text{where } I_\mu = 1/2\ \sigma_\mu$$

We know that $I_\mu^\dagger = I_\mu$ so Hermiticity of ρ requires that $A_{\mu\upsilon}$ = real. What about tr(ρ) = 1? We can write out ρ's matrix elements like this: (using the definition of a direct product matrix)

$$\rho_{\mathbf{ik},\mathbf{j\ell}} = \Sigma_{\mu\upsilon}\ A_{\mu\upsilon}\ (I_\mu)_{\mathbf{ij}}\ (I_\upsilon)_{\mathbf{k\ell}}$$

Then $\mathrm{tr}(\rho) = \rho_{\mathbf{ik},\mathbf{ik}} = \Sigma_{\mu\upsilon}\ A_{\mu\upsilon}\ (I_\mu)_{\mathbf{ii}}(I_\upsilon)_{\mathbf{kk}} = \Sigma_{\mu\upsilon}\ A_{\mu\upsilon}\ \delta_{\mu,0}\,\delta_{\upsilon,0}\ (I_0)_{\mathbf{ii}}(I_0)_{\mathbf{kk}} = A_{00} * 1 * 1 = A_{00}$.
So we conclude that $A_{\mu\upsilon}$ can be an arbitrary 4x4 real matrix but we require that $A_{00} = 1$.

So the set of matrices $I_{1\mu}I_{2\upsilon}$ form a complete basis for expression of ρ with real coefficients. Of course specific elements of the ρ matrix can be complex since I_y is imaginary. In Levitt, we constantly see ρ expressed as various linear combinations of the spin matrices with real coefficients.

Separable Transformations

Now let's apply a (separable) transformation operator to the density matrix. Let's use the sign convention that Levitt uses for example on page 316 for his π_x pulse, or page 368 bottom for the general rotation. We have things like

$$\rho' = R\,\rho\,R^{-1} = (R_1 \otimes R_2)(\rho_1 \otimes \rho_2)(R_1 \otimes R_2)^{-1} = (R_1\rho_1 R_1^{-1}) \otimes (R_2\rho_1 R_2^{-1})$$

Notice that in general R_1 and R_2 can be different transformations. I assume they are unitary I suppose.

Now look at these operators that arise in J-coupling

$$U_{12} = \exp(-i\pi J_{12}\, 2I_{1z}I_{2z}) \qquad U = \exp(-i\,\alpha\, \mathbf{I_1}\bullet \mathbf{I_2})$$

Neither one of these is separable in the sense of $U = U_1 \otimes U_2$. Each term in the infinite exponential sum is separable, so for weak couplings, you could do perturbation theory with separable operators. Note that the two I's commute, that is not the problem here. The problem is each **I** not commuting with itself.

I think this is the reason we have all the complexity in Levitt for the J coupling stuff. I suppose that is the whole point of "J coupling" is that you have coupled the two subspaces, and this forces you do work in the larger 4x4 space.

So OK, let's imagine two different kinds of operators.

(1) Rotations as Separable Transformations. When we talk about something like an "x rotation by π" we, we mean this:

$$R_x(\pi) = R_{1x}(\pi) \otimes R_{2x}(\pi) = \exp(-i\pi I_{1x}) \otimes \exp(-i\pi I_{2x}) = \exp(-i\pi\, I_{1x}{}^{*}\, I_{2x})$$

where we use $I_{1x}{}^{*}\, I_{2x} = (I_{1x} \otimes 1) + (1 \otimes I_{2x})$. We have just quoted a general theorem from my notes which says this:

$$e^{A*B} = e^A \otimes e^B \quad \text{where } A*B \equiv (A \otimes 1) + (1 \otimes B)$$

Does this theorem have a name? The proof is so trivial that it probably does not, I don't have any reference for this other than my notes. Now, in simplified Levitt notation we would write (on the right)

$$I_{1x}{}^{*}\, I_{2x} = (I_{1x} \otimes 1) + (1 \otimes I_{2x}) = I_{1x} + I_{2x}$$

and we would replace this

$$R_x(\pi) = R_{1x}(\pi) \otimes R_{2x}(\pi) = \exp(-i\pi I_{1x}) \otimes \exp(-i\pi I_{2x}) = \exp(-i\pi\, I_{1x}{}^{*}\, I_{2x})$$

with this

$$R_x(\pi) = R_{1x}(\pi)\, R_{2x}(\pi) = \exp(-i\pi I_{1x}) \exp(-i\pi I_{2x}) = \exp(-i\pi\, [I_{1x} + I_{2x}])$$

This kind of operator factorizes, and in each space it is the same rotation. So, when we talk rotations, we can always think this way

$R = R_1 \otimes R_2 = R_1 R_2$ where the rotations are the same, just in the different spaces

For such a factorizing operator, we can compute the effect on ρ as follows:

$$\rho' = R\,\rho\,R^{-1} = (R_1\rho_1 R_1^{-1}) \otimes (R_2\rho_2 R_2^{-1})$$

where the density matrices might be different, but our implication is that $R_1 = R_2$ in the sense of rotations being the same, just in the different spaces. Now we know that

$\rho_1 = 1/2 + \mathbf{a}\bullet\mathbf{I}_1$ // most general traceless form

so

$$(R_1\rho_1 R_1^{-1}) = 1/2 + \mathbf{a}\bullet (R_1\mathbf{I}_1 R_1^{-1})$$

Thus, our "rotated" 4x4 density matrix would have this form:

$$\rho' = R\,\rho\,R^{-1} = 1/4 + 1/2\ [\ \mathbf{a}\bullet\mathbf{I}_1' + \mathbf{b}\bullet\mathbf{I}_2'] + \mathbf{a}\bullet\mathbf{I}_1'\,\mathbf{b}\bullet\mathbf{I}_2'$$

where $\mathbf{I}_1' = R_1\mathbf{I}_1 R_1^{-1}$ and the same for 2. So this is the most general thing that can happen to a density matrix from a pure rotation.

Non-Separable Transformations

Here we get a less simple result:

$$\rho = 1/4 + 1/2\ [\ \mathbf{a}\bullet\mathbf{I}_1 + \mathbf{b}\bullet\mathbf{I}_2] + \mathbf{a}\bullet\mathbf{I}_1\,\mathbf{b}\bullet\mathbf{I}_2$$

$$\rho' = U\,\rho\,U^{-1} = 1/4 + 1/2\ [\ \mathbf{a}\bullet\mathbf{I}_1'' + \mathbf{b}\bullet\mathbf{I}_2''] + U\,(\mathbf{a}\bullet\mathbf{I}_1\ \mathbf{b}\bullet\mathbf{I}_2)\,U^{-1}$$

where $\mathbf{I}_1'' = U\,\mathbf{I}_1\,U^{-1}$ and same for 2. But we can insert $U^{-1}U$ between the two dot products to get our this simpler form

$$\rho' = U\,\rho\,U^{-1} = 1/4 + 1/2\ [\ \mathbf{a}\bullet\mathbf{I}_1'' + \mathbf{b}\bullet\mathbf{I}_2''] + \mathbf{a}\bullet\mathbf{I}_1''\,\mathbf{b}\bullet\mathbf{I}_2''$$

which now looks just like the rotation case.

(1) Non-secular J-coupling. Now consider this situation:

$$U = \exp(-i\,\beta\,\mathbf{I}_1\bullet\mathbf{I}_2)$$

so

$$\mathbf{I}_1'' = U\mathbf{I}_1U^{-1} = \exp(-i\,\beta\,\mathbf{I}_1\bullet\mathbf{I}_2)\ \ \mathbf{I}_1\ \exp(+i\,\beta\,\mathbf{I}_1\bullet\mathbf{I}_2)$$

I went off in a separate document to evaluate this nightmare, here was my result (not checked):

$$\mathbf{I_1}'' = U\mathbf{I_1}U^{-1} = \mathbf{I_1} + \beta\, z^{-1} \sin(z)\, \mathbf{I_1 \times I_2} - \beta^2 z^{-2} D\,[\,1-\cos(z)\,]\,(\mathbf{I_1 - I_2})$$

where $D = \mathbf{I_1} \bullet \mathbf{I_2}$ and $z = \sqrt{2\beta D}$. We can do $\mathbf{I_1} \leftrightarrow \mathbf{I_2}$ to get the similar result for transforming $\mathbf{I_2}$, and the only difference is that the second two terms change sign as is obvious. The above is what you would get if you tried to "propagate" the density matrix using a non-secular J-coupling! You might be able to do something in a small-β limit, but the general case is a true mess. Remember that z is an operator.

(2). Secular J-coupling. Here we have

$$U = \exp(-i\,\beta\, I_{1z}\, I_{2z})$$

In calculation $\mathbf{I_2}'' = U\mathbf{I_2}U^{-1}$, we can think of $U = R_z(\beta I_{2z})$ and use the usual formulas, but we then have $\theta = \beta I_{2z}$ appearing as an operator argument in sinθ and cosθ. But it turns out that this simplifies for spin-1/2 and we get this result (from "the secular J couple expo.doc". See this doc for explanation of how the factors of 2 arise -- basically from $S_z^2 = (1/2)^2$.)

$$\exp(-i\,\phi\, 2L_zS_z)\; L_k \exp(+i\,\phi\, 2L_zS_z) = L_k \cos\phi + \varepsilon_{kmz}\, 2L_mS_z \sin\phi + \delta_{kz}\, L_z\,(1-\cos\phi)$$

which we can translate to read (valid for k = x,y,z)

$$\exp(-i\,\phi\, 2I_{1z}I_{2z})\; I_{1k} \exp(+i\,\phi\, 2I_{1z}I_{2z}) = I_{1k} \cos\phi + \varepsilon_{kmz}\, 2I_{1m}I_{2z} \sin\phi + \delta_{kz}\, I_{1z}\,(1-\cos\phi)$$

If we were to swap $I_1 \leftrightarrow I_2$, we would restore the second term with an index exchange which makes a sign change there, so we would get

$$\exp(-i\,\phi\, 2I_{1z}I_{2z})\; I_{2k} \exp(+i\,\phi\, 2I_{1z}I_{2z}) = I_{2k} \cos\phi - \varepsilon_{kmz}\, 2I_{1m}I_{2z} \sin\phi + \delta_{kz}\, I_{2z}\,(1-\cos\phi))$$

Now, when you have a pair of coupled spins, the Ham is $H' = 2\pi J\, I_{1z}I_{2z}$ so we identify

$$\phi = \pi J t \qquad t = \text{time}$$

Now, when you do a **spin-echo sandwich** as on page 381, you set $\tau = 1/(2J)$ as on page 382, so this means you have

$$\phi = \pi J t = \pi J \tau = \pi/2 \quad = \quad \cos\phi = 0 \quad \sin\phi = 1$$

In this case we get:

$$\exp(-i\,\phi\, 2I_{1z}I_{2z})\; I_{1k} \exp(+i\,\phi\, 2I_{1z}I_{2z}) = \varepsilon_{kmz}\, 2I_{1m}I_{2z} + \delta_{kz}\, I_{1z}$$

For example,

$$\exp(-i\,\phi\, 2I_{1z}I_{2z})\; I_{1x} \exp(+i\,\phi\, 2I_{1z}I_{2z}) = 2I_{1y}I_{2z}$$

$$\exp(-i\,\phi\,2I_{1z}I_{2z})\;\; I_{1y}\;\exp(+i\,\phi\,2I_{1z}I_{2z}) \;\;= -\,2I_{1x}I_{2z}$$

and these are the things you can just read off the pictures on page 377. This would apply if you free-ran for the entire time τ . So in a J-coupling situation, free running without an external RF pulse still "does something" and you get this mixing acting.

So, here is a question of the kind I am trying to understand in this document: suppose you have this kind of coupled U operator active. What does it *do* in general to your density matrix? First, go back and write this:

$$\exp(-i\,\phi\,2I_{1z}I_{2z})\;\; I_{2k}\;\exp(+i\,\phi\,2I_{1z}I_{2z}) \;\;= I_{2k}\cos\phi \;\; - \;\; \varepsilon_{kmz}\,2I_{1m}I_{2z}\sin\phi + \;\delta_{kz}\,I_{2z}\,(1-\cos\phi)$$

$$\exp(-i\,\phi\,2I_{1z}I_{2z})\;\; \mathbf{I_2}\;\exp(+i\,\phi\,2I_{1z}I_{2z}) \;\;= \mathbf{I_2}\cos\phi - 2\,\mathbf{I_1}\times\mathbf{I_2}\sin\phi + \;\hat{\mathbf{z}}\,(\,\mathbf{I_2}\bullet\hat{\mathbf{z}}\,)\,(1-\cos\phi)$$

$$= U\,\mathbf{I_2}\,U^{-1} = \mathbf{I_2}''$$

So we have

$$\mathbf{I_2}'' = \mathbf{I_2}\cos\phi \;-\; 2\,\mathbf{I_1}\times\mathbf{I_2}\sin\phi + \;\hat{\mathbf{z}}\,(\,\mathbf{I_2}\bullet\hat{\mathbf{z}}\,)\,(1-\cos\phi) \qquad\qquad \phi = \pi Jt$$

$$\mathbf{I_1}'' = \mathbf{I_1}\cos\phi + 2\,\mathbf{I_1}\times\mathbf{I_2}\sin\phi + \;\hat{\mathbf{z}}\,(\,\mathbf{I_1}\bullet\hat{\mathbf{z}}\,)\,(1-\cos\phi)$$

$$\rho' = U\,\rho\,U^{-1} = 1/4 \;+ 1/2\,[\;\mathbf{a}\bullet\mathbf{I_1}'' \;+ \mathbf{b}\bullet\mathbf{I_2}''] \;\;+ \;\;(\mathbf{a}\bullet\mathbf{I_1}''\,\mathbf{b}\bullet\mathbf{I_2}'')$$

This, then, is what happens to the density matrix under just this secular J-coupling operator.

Precession for the AX System.

Now, what happens under the simpler part of the Hamiltonians?

$$H' = -\,\gamma_1 I_{1z}\,B^0 \;-\,\gamma_2 I_{2z}\,B^0$$

The first term affects I_1 and we get

$$\exp(-i\,\theta\,\hat{\mathbf{n}}\bullet\mathbf{J})\;\; J_k\;\exp(+i\,\theta\,\hat{\mathbf{n}}\bullet\mathbf{J}) \;\;= J_k\cos\theta \;\; + \;\;[\mathbf{J}\times\hat{\mathbf{n}}\,]_k\sin\theta + \;\hat{n}_k\,(\hat{\mathbf{n}}\bullet\mathbf{J})\;\;(1-\cos\theta)$$

where $\hat{\mathbf{n}} = \hat{\mathbf{z}}$ and $\mathbf{J} = \mathbf{I_1}$ and $\theta_1 = -\gamma_1 B^0\,t$. So we get

$$\mathbf{I_1}'' = U\,\mathbf{I_1}\,U^{-1} \;= \mathbf{I_1}\cos\theta_1 \;\; + \;\;[\mathbf{I_1}\times\hat{\mathbf{z}}\;]\sin\theta_1 + \;\hat{\mathbf{z}}\;\;(\hat{\mathbf{z}}\bullet\mathbf{I_1})\;\;(1-\cos\theta_1)$$

$$\mathbf{I_2}'' = U\,\mathbf{I_2}\,U^{-1} \;= \mathbf{I_2}\cos\theta_2 \;\; + \;\;[\mathbf{I_2}\times\hat{\mathbf{z}}\;]\sin\theta_2 + \;\hat{\mathbf{z}}\;\;(\hat{\mathbf{z}}\bullet\mathbf{I_2})\;\;(1-\cos\theta_2)$$

$$\rho' = U\,\rho\,U^{-1} = 1/4 \;+ 1/2\,[\;\mathbf{a}\bullet\mathbf{I_1}'' \;+ \mathbf{b}\bullet\mathbf{I_2}''] \;\;+ \;\;(\mathbf{a}\bullet\mathbf{I_1}''\,\mathbf{b}\bullet\mathbf{I_2}'')$$

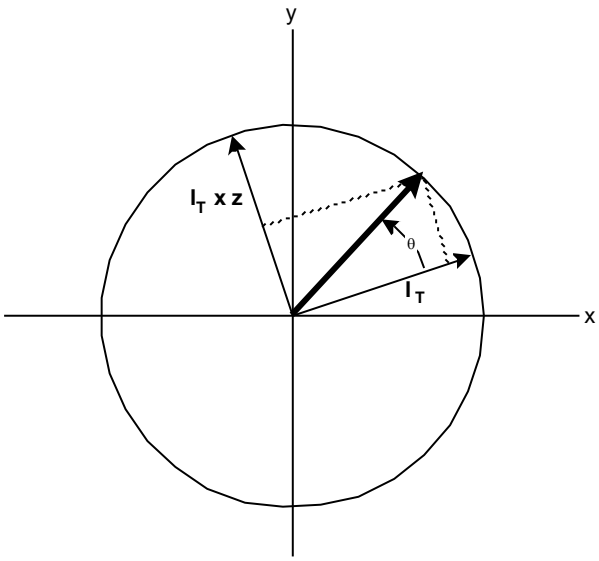
Now, if we have the full Hamiltonian with the J-coupling and the base terms all running and we just free propagate, we get a huge mess, in terms of all this math.

But, suppose we think of $\mathbf{I_1} = (\mathbf{I_{1T}}, \mathbf{I_{1L}})$ having its transverse and longitudinal parts. Then we can write

$\mathbf{I_{1L}}'' = U\,\mathbf{I_{1L}}\,U^{-1} = \mathbf{I_{1L}}$ // nothing happens at all

$\mathbf{I_{1T}}'' = U\,\mathbf{I_{1T}}\,U^{-1} = \mathbf{I_{1T}}\cos\theta_1 + [\mathbf{I_{1T}} \times \hat{\mathbf{z}}]\sin\theta_1$ // rotates

This second equation just describes the constant rotation in time of our transverse vector:



So the simple parts of the Hamiltonian are just causing the spins to *precess*, each at its appropriate chemical shifted frequency. In the rotating frame, we take out this precession effect as best we can.

Of course at TE in a sample, the transverse components average to zero. This means that things just sit there and precess, but averages result in things like this:

$\rho_1 = (1/2 + \mathbf{a}\bullet\mathbf{I_1}) = 1/2 + B_1 I_{1z}/2$ so $\mathbf{a} = (B_1/2)\,\hat{\mathbf{z}}$

$\rho_2 = (1/2 + \mathbf{b}\bullet\mathbf{I_2}) = 1/2 + B_2 I_{2z}/2$ so $\mathbf{b} = (B_2/2)\,\hat{\mathbf{z}}$

and then we get

$\rho = 1/4 + 1/2\,[(B_1/2)I_{1z} + (B_2/2)I_{2z}] + (B_1/2)aI_{1z}\,(B_2/2)I_{2z}$

The precession part of the time propagation then does nothing at all to this ρ, it just sits there. The J-coupling term also does nothing since it is all-z stuff. So ρ just sits there and does nothing! Yes, we have a non-zero Hamiltonian, but in TE when you exponentiate Ham it just does nothing at all. That is why you have to issue some kind of pulse to get the ball rolling.

[At this point, I changed my subscript formatting, imported from normal.dot, and that then changed everything in this document.]

What does the RF pulse do?

It makes a Hamiltonian term [in the rotating frame] of the form $H' = (1/2)|\gamma| B_{RF} I_x$ [see page 260 and 9.25.],where as noted above we can write $I_x = I_{1x} + I_{2x}$. So what happens when we apply such a pulse to the TE density matrix? This is our first case above, so we have this, where $R_i = R_{ix}(\gamma B_{RF} I_{ix} \tau)$ where τ is the pulse duration:

$$\rho' = R\, \rho\, R^{-1} = (R_1 \rho_1 R_1^{-1}) \otimes (R_2 \rho_2 R_2^{-1})$$

But we are starting in TE with

$$\rho_1 = (1/2 + \mathbf{a} \bullet \mathbf{I_1}) = 1/2 + B_1 I_{1z}/2 \quad \text{so } \mathbf{a} = (B_1/2)\, \hat{\mathbf{z}}$$

so we get, defining $\beta_1 = (1/2)|\gamma_1| B_{RF} \tau$, $\hat{\mathbf{n}} = \hat{\mathbf{x}}$ and copying from our "evaluate n•J rotation document",

$$\mathbf{I_1}'' = \exp(-i\theta\, \hat{\mathbf{n}} \bullet \mathbf{I_1})\ \mathbf{I_1}\ \exp(+i\theta\, \hat{\mathbf{n}} \bullet \mathbf{I_1}) = \mathbf{I_1} \cos\beta + \mathbf{I_1} \times \hat{\mathbf{n}} \sin\beta + \hat{\mathbf{n}} (\hat{\mathbf{n}} \bullet \mathbf{I_1}) (1 - \cos\beta)$$

so

$$\mathbf{I_1}'' = R_{2x}(\beta_1) \mathbf{I_1} R_{2x}(\beta_1)^{-1} = \mathbf{I_1} \cos\beta_1 + \mathbf{I_1} \times \hat{\mathbf{x}} \sin\beta + \hat{\mathbf{x}} (\hat{\mathbf{x}} \bullet \mathbf{I_1}) (1 - \cos\beta_1)$$

Now we are interested in

$$\rho_1'' = (1/2 + \mathbf{a} \bullet \mathbf{I_1}'') = (1/2) + (B_1/2)\, \hat{\mathbf{z}} \bullet \mathbf{I_1}'' = (1/2) + (B_1/2)\, I_{1z}''$$

so we take the z component of our expression to get

$$I_{1z}'' = R_{2x}(\beta_1) I_{1z} R_{2x}(\beta_1)^{-1} = I_{1z} \cos\beta_1 - I_{1y} \sin\beta_1$$

since cyclic says $\hat{\mathbf{z}} \bullet [\mathbf{I_1} \times \hat{\mathbf{x}}] = \mathbf{I_1} \bullet \hat{\mathbf{x}} \times \hat{\mathbf{z}} = \mathbf{I_1} \bullet (-\hat{\mathbf{y}}) = -I_{1y}$. We could also find that

$$I_{1y}'' = R_{2x}(\beta_1) I_{1y} R_{2x}(\beta_1)^{-1} = I_{1y} \cos\beta_1 + I_{1z} \sin\beta_1$$

and of course $I_{1x}'' = I_{1x}$. What do these equations tell us?

(1) in the rotating frame where we are working, the spin operator/vector $\mathbf{I_1}$ is rotating in the y-z plane in the positive sense around the x axis.

(2) The density matrix starts out as $\rho_1 = 1/2 + (B_1/2) I_{1z}$ and as time goes by, it is given by

$$\rho_1'' = 1/2 + B_1 I_{1z}''/2 = 1/2 + (B_1/2) [\ I_{1z} \cos\beta_1 - I_{1y} \sin\beta_1\ ]$$

We are saying that, during the RF pulse, ρ_1's second piece *transforms as* the z-component of a vector operator that is rotating in the y-z plane. At t = 0 we start out with $\rho_1 = 1/2 + (B_1/2) I_{1z}$. At $\beta_1 t = \pi/2$

we have $\rho_1" = 1/2 - (B_1/2)I_{1y}$, for example. The density matrix itself is not a vector that rotates; rather, it contains a term that is the z component of a vector that rotates.

Notice that $\rho_1" = 1/2 - (B_1/2)I_{1y}$ has off-diagonal matrix elements.

Apply an RF pulse to a system at absolute zero temperature.

Problem: A spin-1/2 system is in TE at absolute zero. At t=0 we apply an RF pulse. What happens to the expectation value of the system energy?

Solution: Consider the expectation value of energy in our spin system. We have $\langle E \rangle = tr(\rho H)$ where H is the Ham. If we have absolute zero, then $\rho = diag(1,0) = I^{\alpha} = (1/2) + I_z$, everything is in the z=aligned state α. Then if $H = -BI_z$. we get that $\langle E \rangle = tr(\rho H) = -Btr(I^{\alpha} I_z) = -B \{ tr\, I_z/2 + tr\, I_z^2 \}$
$= -B \{ 0 + tr\, (1/4) \} = -B/2.$

Now turn on an RF pulse so we turn on $H = kI_x$. This causes ρ to move in time according to:

$$\rho' = R_x(\beta) I^{\alpha} R_x(-\beta) = R_x(\beta)\{(1/2) + I_z\}R_x(-\beta) = (1/2) + R_x(\beta)\, I_z\, R_x(-\beta)$$

$$= I_z \cos\beta - I_y \sin\beta \qquad \text{where } \beta = (1/2)|\gamma_1|\, B_{RF} t$$

What happens to the energy of our spin-1/2 system during this pulse?

$$\langle E \rangle = tr(\rho' H) = tr(\, \{I_z \cos\beta - I_y \sin\beta\}\{-BI_z + (1/2)|\gamma|\, B_{RF} I_x\}\,)$$

But Dirac says $tr(\sigma_i \sigma_j) = \delta_{ij}$ so among the four terms there is only one contributing term and

$$\langle E \rangle = tr(\, \{I_z \cos\beta\}\{-BI_z\}\,) = -B\cos\beta\, tr(I_z^2) = -(B/2)\cos\boldsymbol{\beta}$$

A very simple result. Now suppose we apply a pulse of 60 degrees so $\cos\beta = 1/2$. Then our pulse has changed the system energy from -B/2 to -B/4. Since our spin system increased in energy, we conclude that it must have absorbed that extra energy "somehow" from the RF pulse field. If we stop the pulse, we expect (ignoring relaxation processes) the spin system to radiate and to return to -B/2.

Now, what happens in the above problem to the transverse magnetization? Roughly we can say that

$$\langle M_t \rangle = \text{const} * tr(\rho \{ I_x \hat{\mathbf{x}} + I_y \hat{\mathbf{y}} \}) \sim \hat{\mathbf{x}}\, tr(\rho I_x) + \hat{\mathbf{y}}\, tr(\rho I_y)$$

$$= \hat{\mathbf{x}}\, tr(\{ I_z \cos\beta - I_y \sin\beta\} I_x) + \hat{\mathbf{y}}\, tr(\{ I_z \cos\beta - I_y \sin\beta\} I_y)$$

$$= -\hat{\mathbf{y}} \sin\beta\, tr(I_y^2) = -\hat{\mathbf{y}}\, (1/2)\sin\beta$$

So this starts at 0, then is a sine pattern in the $-\hat{\mathbf{y}}$ direction as shown where $\beta = (1/2)|\gamma_1|\, B_{RF} t$. Of course in the non-rotating frame, this thing is precessing like mad, and since all spins are aligned at this point, we get radiation by the accelerating magnetic dipole moment, and that removes the energy our pulse put in. The idea of having a "strong" pulse, is that we can ignore this radiation *during* the pulse.

So field-classically, we understand that the spin system energy increases by absorbing energy from the RF pulse, then when the pulse stops, we expect to have radiation with energy given back to an EM field and that is the NMR signal. It is implicit in the above that the RF pulse has the perfect resonant frequency and phase so we have this simple I_x Ham in the rotating frame. We expect the radiated energy to have the same frequency, since it is roughly DC in the rotating frame.

From a quantum field viewpoint, during the initial pulse the system is absorbing photons at some rate, and as these are absorbed, the energy <E> gradually increases from -B/2 to -B/4 as shown above. At the end of a $\pi/2$ pulse, we have <E> = 0 and we have equalized our populations. The spin system then gradually emits photons and goes back to energy -B/2, and the emitted photons are the NMR signal.

Now, for this system, how can we "interpret" the off diagonal elements of ρ? More on this in the next section, but, since $<M_t>$ = const * tr(ρ { $I_x \hat{\mathbf{x}} + I_y \hat{\mathbf{y}}$ }), if ρ is diagonal, having the form $A + BI_z$, then we will have $<M_t>= 0$ and there will be no radiation so no NMR signal. So somehow the NMR signal *requires* a non-vanishing off-diagonal element of ρ.

Point of Confusion. Suppose you apply a $\pi/2$ pulse and you tip the rotating-frame magnetization down from z to the -y direction. We speak of the relaxation times T_1 and T_2 and we put exponential decay factors into the ρ propagation. Is radiation part of these? If these constants were infinite, the models used in the book would say that the NMR signal would go on forever. So perhaps this radiation loss is included as part of the model for T_1 and/or T_2. Levitt has not addressed this point so far in his book.

Here is a comment from the web which, if correct, provides the answer:

"How do nuclei in the higher energy state return to the lower state? Emission of radiation is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. We must focus on non-radiative relaxation processes (thermodynamics!)."

What is the meaning of an off-diagonal matrix element in ρ ?

A. Opening Comments

Example #1. We know that $\rho = \Sigma_\alpha |\alpha> p_\alpha <\alpha|$ where we are summing over an ensemble of states. Suppose for simplicity there is only one state α in this ensemble. Then we have $\rho = |\alpha><\alpha|$ which is just the projection operator onto this state. Then consider an off-diagonal matrix element of ρ:

$$<i|\rho|j> = <i|\alpha><\alpha|j>$$

where the i and j states represent energy eigenstates. If $|\alpha>$ is also an energy eigenstate, then it cannot be in both i and j, so we find that $<i|\rho|j>= 0$. This would also be true in the ensemble if all the $|\alpha>$ states were energy eigenstates.

Therefore, if $<i|\rho|j> \neq 0$, it means that at least some states $|\alpha>$ in the ensemble are not in energy eigenstates. Now from our Stern-Gerlach document, we know that we can form a linear combination of energy eigenstates for a spin-1/2 system, and that such a state is not an energy eigenstate. For a spin-1/2 system in such a state, we would have, for example

$\langle 1|\rho(0)|2\rangle = \langle 1|\alpha(0)\rangle\langle\alpha(0)|2\rangle = ab^* \neq 0$

so here is a situation where we have prepare a system in a state such that the density matrix has an off-diagonal matrix element (relative to a z axis, so to speak). The spin-1/2 object might be in vacuum and so have no Hamiltonian and this ρ_{12} element does not change in term at all. So I put up this example just to claim that you can have an off-diagonal ρ matrix element and it has nothing to do with any transitions between states 1 and 2.

Example #2. Consider the single spin-1/2 system. The off diagonal matrix ρ element is this:

$\langle\alpha|\rho|\beta\rangle \neq 0$ which says that $\Sigma_n \langle\alpha|n\rangle p_n \langle n|\beta\rangle \neq 0$

where n are the ensemble states now. If all these states were energy eigenstates, then we would get 0 for our off-diagonal elements, so *at least some* must not be. One way to have the system not be in an energy eigenstate is to have some perturbation Hamiltonian acting, and in this case we can associate off-diagonal matrix elements of ρ with transitions.

Consider Levitt's example with the two spin-1/2's per molecule, the AX system. In this case, we have four spin states and ρ is a 4x4 matrix. We can then ponder off-diagonal states like this:

$\langle\alpha\alpha|\rho|\beta\beta\rangle \neq 0$ which says that $\Sigma_n \langle\alpha\alpha|n\rangle p_n \langle n|\beta\beta\rangle \neq 0$

Again, there must be *at least one* state $|n\rangle$ that contains a mix of $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$ and this state might therefore be involved in a transition affecting the $\alpha\alpha$ and $\beta\beta$ states. Generally all the states in the ρ sum are going to be non-energy-eigenstates.

Transition Theory. Suppose there is a small perturbation term active in the Hamiltonian, such as during an RF pulse. We then know that our states like $|\alpha\rangle$ and $|\beta\rangle$ are no longer eigenstates, and we know that

$|\alpha(t)\rangle = \exp^{-iHt}|\alpha(0)\rangle$ where $H = H^0 + H'$

Whereas the H^0 will merely phase the state, the H' will cause a rotation, so we get

$|\alpha(t)\rangle = e^{-iE_\alpha t} \exp^{-iH't}|\alpha\rangle = e^{-iE_\alpha t} |i\rangle\langle i| \exp^{-iH't}|\alpha(0)\rangle$

$= \text{const} * U_{i\alpha}(t) |i\rangle$ = a mix of eigenstates.

The amplitude that this state $|\alpha(t)\rangle$ is in energy eigenstate $\langle n|$ is given by

$\langle n|\alpha(t)\rangle = \text{const} * U_{n\alpha}(t)$

so the state $|\alpha(t)\rangle$ will be "departing" or "entering" state $|n\rangle$ over time, meaning we have transition activity going on.

Meanwhile, the density matrix looks like $\rho = \Sigma_\alpha |\alpha\rangle p_\alpha \langle\alpha|$ where we sum over an ensemble of states like our state $|\alpha(t)\rangle$. Suppose there is only one state in the ensemble , $|\alpha(t)\rangle$. Then we have

$\rho(t) = |\alpha(t)><\alpha(t)|$ and

$<m|\rho(t)|n> = <m|\alpha(t)><\alpha(t)|\ n> = \text{const x } U_{m\alpha}(t)\ [\ U_{n\alpha}(t)]^{*} \neq 0.$

This is not zero because it is reasonable to assume that $|\alpha(t)>$ has some amplitude to be in both states m and n, generally speaking. If there were no perturbation term, we could not say this. We can then average this idea over the ensemble to say

$$<m|\rho(t)|n> = \Sigma_{\alpha}<m|\alpha(t)>p_{\alpha}<\alpha(t)|\ n> = \Sigma_{\alpha}\ p_{\alpha}\ \text{const x } U_{m\alpha}(t)\ [\ U_{n\alpha}(t)]^{*} \neq 0.$$

So now let's say this a different way. Suppose we know that $<m|\rho(t)|n> \neq 0$. Then we know that at least some states in the ensemble "have a foot in both states m and n." We have seen above how a perturbation Hamiltonian can cause exactly this to happen. Here is more on that subject:

B. Perturbation theory and Transition Rate

We know that

$$\rho(t) = U(t)\ \rho(0)\ U(t)^{-1} \qquad U(t) = \exp^{-iHt}$$

Let's assume that H^0 has no effect on the $\rho(0)$ we happen to start with, so $H \rightarrow H'$ in the above. We can then do this expansion: [perhaps we do this in the "interaction picture" to remove H^0]

$$\rho(t) = (1 - iH't)\ \rho(0)\ (1 + iH't) = \rho(0) - it\ [H', \rho(0)] + \ldots$$

Then write:

$$<m|\rho(t)|n> = <m|\rho(0)|n> - it\ <m\ |\ [H', \rho(0)]\ |n>$$

For the moment ignoring the first term, we have

$$\begin{aligned} <m|\rho(t)|n> &= -it\{\ <m\ |\ H'|k><k|\rho(0)\ |n> - <m\ |\ \rho(0)|k><k|H'\ |n> \\ &= -it\ \{\ H'_{mn}\ <n|\rho(0)\ |n> - <m|\ \rho(0)|m>\ H'_{mn} \\ &= -it\ H'_{mn}\ \{\ \rho(0)_{nn} - \rho(0)_{mm}\ \} \end{aligned}$$

Finally we get something interesting (which Levitt did write somewhere). So we have proved:

Theorem: Assume that $tH' << 1$ during our RF pulse. Then to first order we can say

$$\rho(t)_{mn} = \rho(0)_{mn} - it\ H'_{mn}\ \{\ \rho(0)_{nn} - \rho(0)_{mm}\ \}$$

This makes a direct connection between the off-diagonal elements of the density matrix, known as coherences, and off-diagonal matrix elements of the interaction Hamiltonian. The larger this H' matrix element, the larger will be the interesting term in $\rho(t)_{mn}$. Secondly, this term is also proportional to the

population difference between our two states of interest at time 0. Thus we can unequivocally associate a coherence with an off-diagonal H' matrix element and therefore with a "transition" between the two states n and m. This then justifies Levitt's various arrow pictures.

We can of course generalize the above away from time 0 and say

$$\rho(t+\Delta t)_{mn} = \rho(t)_{mn} - i\,\Delta t H'_{mn} \{ \rho(t)_{nn} - \rho(t)_{mm} \}$$

which really says

$$d\rho_{mn}(t)/dt = - i\, H'_{mn} \{ \rho(t)_{nn} - \rho(t)_{mm} \}$$

which says that the interaction Hamiltonian changes the matrix element $\rho_{mn}(t)$ in this manner, and the thing on the right is called the transition rate.

Now consider the AX system with its four states. Suppose m = $\alpha\alpha$ and n = $\beta\beta$. Then $\rho(t)_{mn}$ describes a transition between these two states. Since photons are coming in near the single-gap frequency, this transition would probably have to be a "two photon" transition. Each spin absorbs a photon at the same time. Total number of photons absorbed is 2, so this is a "two quantum coherence". In the case m = $\alpha\beta$ and n = $\beta\alpha$, we again have a two photon event, but one is absorbed and one is emitted at a slightly different frequency because these levels are slightly split. This is called a "zero quantum" coherence because the net number of photons absorbed or emitted is 0. Levitt makes this much more mysterious than it has to be.

Conclusion: An interaction Hamiltonian term H'_{mn} causes a *change* in the ρ_{mn} matrix element, and this change is associated with an RF photon transition between states |m> and |n>. When you start a process in TE at t=0, you always have $\rho(0)_{mn}$= 0 and ρ is diagonal. Then the H'_{mn} causes a non-zero value of $\rho(t)_{mn}$ to develop.

So, all of Levitt's little "coherence diagrams" really are directly related to photon transitions.