The Density Matrix PhL 12.13.07

What is the density operator? // Schiff and Levitt review

Part I:

First, we need to study the notion of "projection operators" as described page 166 Schiff. Imagine you have some operator Ω which has eigenstates $|\mu\rangle$ and assume μ are the eigenvalues of these states. That is, we label the states by their eigenvalues, as for example in the angular momentum notation.

Let states $|i\rangle$ be eigenstates of H.

Define $P_\mu = |\mu\rangle\langle\mu|$. Then

$$\Omega\ [\ P_\mu\ |i\rangle\ ] = \Omega|\mu\rangle\langle\mu|i\rangle = \mu\ |\mu\rangle\langle\mu|i\rangle = \mu\ [\ P_\mu\ |i\rangle\ ].$$

This says that P_μ projects out of state $|i\rangle$ that portion which is an eigenstate of Ω with eigenvalue μ.

Now, suppose we make a state ψ which is "mixed" in that it is a mixture of eigenstates of Ω. All we really know is the probability that ψ is in each of the μ eigenstates, that being p_μ. We could then define an operator ρ as the sum of all projection operators over all Ω states, but weighted by the probability of being in that Ω state, so now we are talking about some kind of *mixed statistical* state:

$$\rho = \Sigma_\mu\ p_\mu\ P_\mu$$

So, if we abstractly ask what matrix element of ρ is, we get this:

$$\langle i|\rho|j\rangle = \Sigma_\mu\ p_\mu\ \langle i|\ P_\mu|j\rangle = \Sigma_\mu\ p_\mu\ \langle i|\mu\rangle\langle\mu|j\rangle = \Sigma_\mu\ \langle i|\mu\rangle p_\mu\langle\mu|j\rangle$$

For each of the Ω eigenstates, we compute the amplitude that said state μ is in state i, and is in state j. We multiply by the probability of being in state μ, and then sum over all the μ states. Somehow, this is the total "flow from state j to state i" through all states μ, but weighted by the probability of state μ being in our mixed state. If all states were *equally weighted*, and say there were N of them, then you would say:

$$\langle i|\rho|j\rangle = \Sigma_\mu\ \langle i|\mu\rangle p_\mu\langle\mu|j\rangle = (1/N)\ \Sigma_\mu\langle i|\mu\rangle\langle\mu|j\rangle = (1/N)\ \langle i|j\rangle = (1/N)\ \delta_{i,j}$$

where I assume N states μ are complete. So if all probabilities for the state μ are the same, then the density matrix is diagonal and $tr(\rho) = 1$ as often claimed.

If the probabilities of the Ω states are not equal, then you start picking up off diagonal elements of matrix ρ. For example, suppose we are entirely in some state μ_1 of Ω in out mixed state. Then we get

$$\langle i|\rho|j\rangle = \Sigma_\mu\ \langle i|\mu\rangle p_\mu\langle\mu|j\rangle = \langle i|\mu_1\rangle\langle\mu_1|j\rangle$$

Aha! This is the "overlap amplitude" between states i and j with respect to this state $\mu 1$. The off diagonal matrix element of ρ is telling you the size of this overlap amplitude! If there is an 0.8 amplitude that state j is in $\mu 1$, and if there is an 0.9 amplitude that i is in $\mu 1$, then there is an 0.72 amplitude that states j and i

are "coupled" through state μ1, or that they "overlap via μ1". In our example, all was through state μ_1, but in general you add of the overlap or flow through all the μ states weighting by p_μ .

Comment on Part I: In the discussion above, we were dealing with two operators H and Ω, and the eigenstates were |i> and |μ> respectively. We thought about some state ψ that was not in an eigenstate of Ω but was a linear combination of eigenstates. In such a situation, we know how to compute the p_μ for being in each eigenstate. We could go another step and think of ψ as some kind of statistical average state of some ensemble where perhaps the linear combination coefficients vary over the ensemble but have some average values.

Part II.

We now shift to page 379 of Schiff. In the earlier section, Schiff never mentions an operator ρ, but I made one up in the Part I discussion above. The early Schiff section was just talking about projection operators.

Now, let's imagine a state ψ of some system that is not in an energy state, but it is in a pure state, which means a definite linear combination of eigenstates. Let's call this state ψ_1. But now imagine a number of these systems ψ_2, ψ_3 and so on which are in different pure states. We want to talk about the "average state". Our motivation is some physical situation like the spins in an NMR sample. You could I suppose just average all the vector kets ψ_1 , ψ_2 and so on, but I don't thing this is one. For each state, we certainly know the probability that it is in each of the eigenstates of H, the square of the coefficients of the linear combination. We could average these to get ensemble averages for these "populations", as Levitt calls them.

Now consider the following "density operator" which we define as in Part I as a weighted sum of projection operators where now the sum is NOT over the eigenstates of some other operator Ω, but is instead over the states of systems in our statistical ensemble -- perhaps there are N such systems.

$$\rho = \Sigma_\psi |\psi> p_\psi <\psi|$$

We talk about a "mixed state" which is somehow the average of all the states in our ensemble. In theory, we could make such a mixed state with unequal weights in the various systems, but in practice all states in the ensemble have the same weight for our average, so we write $p_\psi = 1/N$ and take it outside the sum

$$\rho = (1/N) \Sigma_\psi |\psi><\psi|$$

where again, the sum is over the ensemble. This is what you see top of page 275 in Levitt.

Now let's jump to Levitt page 344. First, we think of a single state ψ which is in fact a direct product state of two spin-1/2 systems, and the four Hamiltonian H eigenstates we call αα αβ βα and ββ and this is how we enumerate the rows and columns of 4x4 matrices. Our single state is not an eigenstate, but it is a pure state that is just a linear combination with things like $c_{\alpha\beta}$ as a typical coefficient. We can at any time define an ensemble by increasing from N=1 to some large N, and then we are talking about a mixed state.

Now, let's think about the matrix elements of this animal ρ. Let's just label the H eigenstates |i> where in this case perhaps i = 1,2,3,4 to enumerate our four direct product states. Then we have:

$$<i|\rho|j> = (1/N) \Sigma_\psi <i|\psi><\psi|j> = [<i|\psi><\psi|j>]_{average}$$

So, this matrix element is the same as discussed in Part 1. If the amplitude $\langle\psi|j\rangle = .9$ for some state ψ in the ensemble, and if $\langle i|\psi\rangle = .8$ for that same state, then the contribution to the average is .72 and this is the contribution to the density matrix. So each term is the "amplitude that states j and i overlap through state ψ", and we just take the average of these terms over the ensemble. Of course the diagonal elements are clearly the populations, the average of $|\langle i|\psi\rangle|^2$ over the ensemble.

Let's try a spin-1/2 example. Suppose ψ = equal mix of up and down with $1/\sqrt{2}$ coefficients. And suppose i = up and j = down. then for this state, $\langle i|\psi\rangle\langle\psi|j\rangle = 1/\sqrt{2} * 1/\sqrt{2} = 1/2$. This then is the amount of "overlap". It is not a transition probability from up to down. You get this same overlap for all four combinations of i and j in this example.

So all I can say is that an off-diagonal i,j matrix element of ρ is the average over the ensemble of the "overlap product amplitude" $\langle i|\psi\rangle\langle\psi|j\rangle$, and Levitt calls such a thing a "coherence" between states i and j and he represents them by arrows.

Part III Spin 1/2 example

What do these coherences do in Levitt? In the spin-1/2 case on page 281, I showed that

$$\langle \mathbf{M}\rangle \sim \langle \mathbf{I}\rangle = \mathrm{tr}(\mathbf{I}\rho) \qquad \text{for example } \langle M_x\rangle \sim \langle I_x\rangle = \mathrm{tr}(I_x\rho) = \mathrm{Re}(\rho_{1/2,-1/2})$$
$$\langle M_y\rangle \sim \langle I_y\rangle = \mathrm{tr}(I_y\rho) = \mathrm{Im}(\rho_{1/2,-1/2})$$

So if I were to define $M_+ = M_x + i\,M_y$ then $\langle M_+\rangle = \mathrm{Re}(\rho_{1/2,-1/2}) + i\ \mathrm{Im}(\rho_{1/2,-1/2}) = \rho_{1/2,-1/2}$. So in this example at least we have an interpretation of this particular coherence: It is a measure of the "complex transverse magnetization".

Let's now review what Levitt does. He goes to thermal equilibrium and says the ρ matrix is diagonal.

At this point, we have to look back to Chapter 9 on "spin-1/2 system" and on page 249 we learn what the time dependence of a state is from the SE. So we know that we need to "exponentiate the Hamiltonian". For example, for the Ham shown page 249 which is just ωI_z, we get (9.10) telling us how things move. The exponentiated thing always involves spin matrices so we call it a "rotation".

Now when we apply the RF pulse, the Ham starts showing I_x and I_y terms as shown page 250 (9.22). This just comes from $\mu \bullet B_{RF}$ and we keep only one circular component. It is convenient then to write this more compactly as shown line below (9.22) so that $H' = R\ I_x\ R^{-1}$ where the angle is that shown in 9.22, just the time argument of our B_{RF} sines and cosines.

So far so good, now go to page 260. Top of page shows our Ham again where we go back to the original form with I_x and I_y weighted by time sine and cosine. We can now select time durations to pick off only the I_x or I_y terms. If our pulse has $\phi_p = 0$, then $H' = \omega_{nut}\ I_x$ and then THIS is what we have to exponentiate to move a state in time. We can then see what this does to our up and down spin states. For example, it flips the +z state to a -y state.

Now go to page 287 and ask: "what happens to the ρ operator as we move in time?" Since the ρ operator is just $(1/N)\ \Sigma_\psi\ |\psi\rangle\langle\psi|$, we are not surprised to get result 10.27 which says that whatever expo Ham moves your state, that thing appears twice on the two sides, once with negated argument.

Now comes the main point: as we apply a B_{RF} pulse, it puts I_x and I_y terms into the Ham H', so when we expo the Ham, we will have x and y rotations. These then act on the matrix ρ to move it in time, and if you start off in TE with zero off-diagonal elements, you end up with some non-zero off-diagonal elements. In other words, the coherences become non-zero at later points in time. In our particular spin-

1/2 case, we know that this means that the B_{RF} pulse is causing a transverse magnetization M. When we stop the pulse, we know that we are back to just I_z and thus the coherence rotates in time and the M vector rotates with it. This thing of course radiates and makes an NMR signal which contributes to the relaxation.

We then turned to page 585 and we realize that since M_x is moving in time, it makes a flux in our readout coil, and we end up with a signal proportional to the coherence as shown page 587.

Part IV The case of two spin-1/2's (per molecule)

So now we go to our direct product state representation with H eigenstates like $\alpha\alpha$. We now have a 4x4 ρ matrix with rows and columns labeled in this order: 1/2,1/2 1/2,-1/2 and so on, with $\alpha\beta$ notation. The meaning of an off-diagonal is still of course "the overlap through state ψ, averaged over the ensemble". The arrows in the diagrams are used to mark this overlap.

Before the RF pulse is applied, we have the "all-z Hamiltonian" shown in 12.9 page 349. When we expo the Ham, we get bottom of page 350, and this "rotation" is then what will make ρ move in time, and all that happens is 12.11, the ρ matrix components just phase in time with difference frequencies. Levitt on page 352 then makes up symbols for each of these phasing frequencies.

Now, oddly, rather than watch what various RF pulses do, Levitt suddenly makes the claim shown top of page 353 for the NMR signal after some pulse sequence, and he claims that four of the 6 coherences contribute to this and you get four lines. I certain could imagine that all 6 coherences become zero when you apply an RF pulse. The unanswered question here is : "why do these four terms contribute and why with simple addition as shown". The whole basis of appendix 17.7 was to claim that the magnetization was inducing a voltage in the pickup coil, so how does that apply here? Levitt has not even mentioned M so far. He has, as usual, left a gaping hole in his presentation.

So he has left me with a problem.

Part V

When you have a system of two direct product spins, what is the magnetization vector? Presumably,

$$\langle \mathbf{M} \rangle \sim \langle \mathbf{I} \rangle = \mathrm{tr}(\mathbf{I}\rho)$$

The RF pulse is going to introduce I_x and I_y terms in H' just as before, but now we have the 4x4 versions. So let's look at some of these.

$$\mathrm{tr}[\, I_x\rho \,] = \mathrm{tr}\left[\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & a \\ 0 & 0 & b & 0 \\ 0 & c & 0 & 0 \\ d & 0 & 0 & 0 \end{pmatrix} \right] = a + b + c + d$$

But these are not the ones with the single - sign! [the left matrix is $I_{1x} \otimes I_{2x}$ which is not the one we want, see below.]

Let's now instead assume that our interaction Ham is more like $-\mu_1 \bullet B_{RF} \; -\mu_2 \bullet B_{RF}$ so then we pick up terms like $I_{1x} \otimes 1$ and $1 \otimes I_{2x}$. The first of these matrices looks like:

$$I_{1x} \otimes 1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\mathrm{tr}[I_{1x} \otimes 1\ \rho\ ] = \mathrm{tr}\left[\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & a & 0 \\ 0 & 0 & 0 & b \\ c & 0 & 0 & 0 \\ 0 & d & 0 & 0 \end{pmatrix} \right] = a + b + c + d = +\alpha + +\beta + -\alpha + -\beta$$

so now we are picking off the right terms. If I use $1 \otimes I_{2x}$, the result is $\alpha+ + \alpha- + \beta+ + \beta-$ and this picks up all the other single-photon terms. Now our two μ's don't have equal weights because there is a chemical shift between them, so I cannot just assume $(I_1 + I_2) \bullet B_{RF}$.

But nevertheless, at this point I have shown that

$\langle M_x \rangle \sim \langle I_x \rangle = \mathrm{tr}(I_x \rho)$ = sum of all 8 single-photon terms.

So then this looks like page 585 equation (17.22) except instead of one pair we have four pairs. We then send the four pairs through the quad receiver machinery, and we will then end up with exactly as Levitt claims on page 353.

In a little more detail now: we know that M_x gives the sum shown page 585, and I just did M_x above and for the four pairs, so that just plain clinches it. I know that the M_x is proportional to the sum of the four pairs of single-photon coherences. What I don't know is what the OTHER coherences are! I saw above how they got picked out by my $I_{1x} \otimes I_{2x}$ term, but I don't think such a term is created by an RF pulse.