Spring 2-1-2007

Density Matrix

Ronald Lovett
Washington University in St. Louis

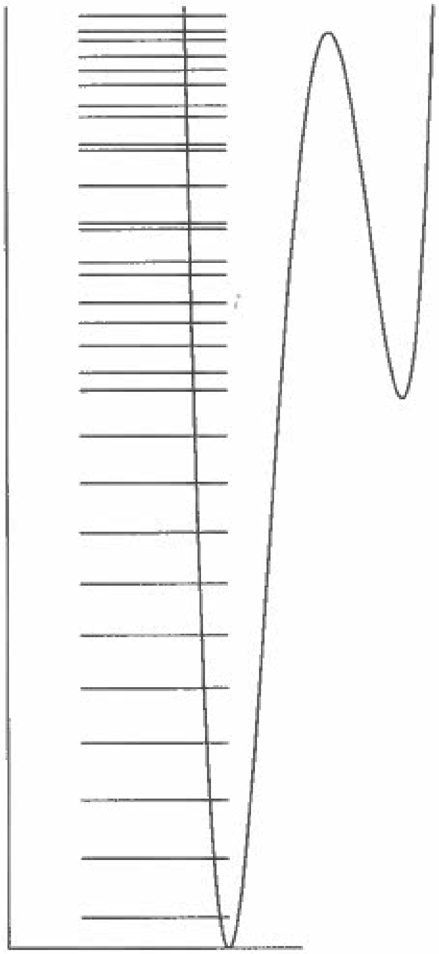
Recommended Citation

Lovett, Ronald, "Density Matrix" (2007). *Topics in Quantum Mechanics*. 37.
https://openscholarship.wustl.edu/chem_papers/37

THE DENSITY MATRIX

A. The Problem

1. *I made a calculation for DGS*



I determined the energy eigenfunctions and eigenvalues $\{\psi_n, E_n\}$ for the one-dimensional system with Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

using the double well potential shown at right. Then using electrical units in which the charge of the particle at x was 1, I calculated the dipole moment matrix elements

$$d_{mn} = \langle \psi_m | x | \psi_n \rangle$$

and the first order transition rates

$$k_{mn} = \frac{2\pi}{\hbar} |d_{mn}|^2 \, \rho(E_n).$$

Let $p_n(t)$ be the probability of occupancy of ψ_n at time t. I determined these probabilities by solving

$$\frac{d\,p_n(t)}{dt} = \sum_{m>n} k_{nm}\, p_m(t) - p_n(t) \sum_{m<n} k_{nm} \qquad (1)$$

with the initial conditions $p_n(0) = \delta_{nN}$.

That is, I determined the probability of seeing the system in ψ_n, for all n, at time t, given that $\psi(0) = \psi_N$.

2. *A critique*

In the notes for a course given at the U. Chicago, Fermi labeled a calculation of Pauli as a "golden rule." Superficially, my calculation was an application of *Fermi's Golden Rule I*.

The calculation of Pauli addressed a difficult question: How can one explain a first order (irreversible) decay using a quantum mechanical apparatus that is time reversal invariant? The same question comes up in statistical mechanics: How can a system started in any particular state relax to "thermodynamic equilibrium"?

Pauli considered a system with Hamiltonian

$$\hat{H} = \hat{H}_{matter} + \hat{H}_{field} + \hat{V}. \tag{2}$$

He used time dependent perturbation theory to work out the state of the matter $\psi(t)$ at time t, assuming that the matter-field coupling was weak and that the system was started in $\psi(0) = \psi_i$. From the result he calculated

$$\left|\left\langle \psi_f \middle| \psi(t) \right\rangle\right|^2 = \frac{2\pi}{\hbar} \left|V_{fi}\right|^2 \rho(\mathcal{E} + E_f - E_i)\, t + \cdots$$

with higher order terms having higher powers of the matrix elements of $\hat{V}$ and higher powers of t. There is supposed to be a continuum of *field* states that are coupled to the matter (V_{fi} being the magnitude of the coupling) and $\rho(\mathcal{E} + E_f - E_i)$ is the density of these states. Writing $\left|\left\langle \psi_f \middle| \psi(t) \right\rangle\right|^2 = k_{fi}\, t + \cdots$ identifies the first order rate constant k_{fi}.

But there are several questions that suggest that this calculation is not applicable to DGS's problem.

1° Where does this evaluation of $\left|\left\langle \psi_f \middle| \psi(t) \right\rangle\right|^2$ apply? Only where $k_{fi}\, t \ll 1$. Only when the system is only slightly perturbed. But DGS wants the ψ_N component to go to zero and many intermediate state components rise and fall to zero before the experiment is complete.

2° What is the *initial state* in these calculations? If the ψ_n component grows in time, the assumption is that we can calculate how rapidly it jumps into lower energy states by using a calculation in which $\psi(0) = \psi_n$. That is, a collection of calculations based on initial conditions that *are not realized by the actual experiment* are used to determine the dynamical equation (1).

In fact, for $t > 0$, the state is a complicated superposition of the ψ_n components. In general,

$$\psi(t) = \sum_{n=0}^{N} c_n(t)\, \psi_n \tag{3}$$

Most $|c_n(t)|^2$ never become large. Since the rate calculations are not made for the actual circumstances of the experiment, it is not obvious that the calculated rates apply to the real experiment. Shouldn't interference between various terms lead to transition rates that *change* in time?

3° When is the "measurement" made? The justification for looking at $\left|\left\langle \psi_f \middle| \psi(t) \right\rangle\right|^2 = |c_f(t)|^2$ is that this gives the probability that the system appears to be in state ψ_f *if an observation of the state* is made at time t. But, if the system is *observed* to be in state ψ_f at time t, the observer has changed the state. The rules for the subsequent time evolution would change.

Thus (1) would only apply if the state of the system were continuously being measured, and *an ensemble of repetitions of the experiment* was described statistically with the $p_n(t)$. Again, this is not the actual experiment.

4° Does the matter have a state? The Hamiltonian (2) contains both matter and field coordinates. It is, after all, the field coordinates that are actually observed. Suppose $\{\psi_n\}$ are eigenfunctions of $\hat{H}_{matter}$. To provide a complete description of the system, it is necessary to describe the field. So suppose that $\left\{\Phi_q\right\}$ are energy eigenfunctions of $\hat{H}_{field}$, with "q" some labeling scheme for field states. Then the set of functions $\left\{\psi_n\,\Phi_q\right\}$ provides a basis set for the states of the *system*. In general, the state of the system can be written

$$\Psi = \sum_{q,n} C_{qn}\,\psi_n\,\Phi_q \tag{4}$$

If we start the matter in state ψ_N and the field in state Φ_0, then

$$\Psi(0) = \psi_N\,\Phi_0$$

and it is clear that all properties of the matter are determined by ψ_N.

But time evolution maps $C_{nq} = \delta_{nN}\delta_{q0} \longrightarrow$

$$C_{nq}(t) = \delta_{nN}\delta_{q0}\,e^{-i(E_n+\mathcal{E}_q)t/\hbar} - \frac{i}{\hbar}\sum_{m,r} V_{nq,mr}\int_0^t d\tau\,C_{mr}(\tau)\,e^{-i(E_n+\mathcal{E}_q)(t-\tau)/\hbar}$$

In $t > 0$, it is impossible to write (4) in the form $\psi(t)\,\Phi(t)$, so there is no "state function." from which the properties of the matter can be deduced. This is the "entanglement" problem.

B. The Example of Statistical Mechanics

1. *The standard argument*

Suppose we're looking at some mechanical system with Hamiltonian $\hat{H}$ and we know the solutions to

$$\hat{H}\,\psi_i = E_i\,\psi_i.$$

What is the "expectation" of some mechanical quantity $\hat{Q}$ of this system when the system is thermostated at a temperature T? The *canonical answer* is

$$\langle Q\rangle = \sum_{\text{states } i} Q_{ii}\,e^{-\beta E_i} \Big/ \sum_{\text{states } i} e^{-\beta E_i} \tag{5}$$

with $\beta = 1/k_BT$ and $Q_{ii} = \langle\psi_i|\hat{Q}|\psi_i\rangle$.

If the system were in a state like (3), the expectation of $\hat{Q}$ would be

$$\langle Q\rangle = \sum_{i,j} c_i^* \, Q_{ij} \, c_j. \tag{6}$$

This is not the same prediction: The properties attributed to a system at equilibrium are not the properties associated with some particular "state function."

Let

$$e^{-\beta A(T,V,N)} = \sum_{\text{states } i} e^{-\beta E_i} = \sum_i \left\langle \psi_i \left| e^{-\beta \hat{H}} \right| \psi_i \right\rangle = \mathrm{Tr}\left[e^{-\beta \hat{H}}\right]$$

represent the canonical partition function. Then (5) can be rearranged to

$$\begin{aligned}\langle Q\rangle &= \sum_{\text{states } i} Q_{ii} \, e^{\beta(A-E_i)} = \sum_i e^{\beta(A-E_i)} \langle \psi_i|\hat{Q}|\psi_i\rangle \\ &= \sum_i \langle \psi_i | e^{\beta(A-\hat{H})} \, \hat{Q} | \psi_i\rangle \\ &= \mathrm{Tr}\left[e^{\beta(A-\hat{H})} \, \hat{Q}\right]\end{aligned} \tag{7}$$

The trace (7) can be calculated in any basis set. Thus there is an (Hermitian) *operator*

$$\hat{\rho} = e^{\beta(A-\hat{H})} \tag{8}$$

from which all equilibrium properties can be deduced. von Neuman called $\hat{\rho}$ the *density matrix*. A matrix representation of $\hat{\rho}$ in a basis set of energy eigenfunctions gives

$$[\hat{\rho}]_{mn} = \delta_{mn} \, p_n$$

with p_n the weight ($\sim$ probability) of the state ψ_n in the canonical ensemble. Obviously

$$\mathrm{Tr}[\hat{\rho}] = 1. \tag{9}$$

In general, von Neuman argued, a complete characterization of any "statistical ensemble" would require a density matrix. Generally, if $\{\varphi_i\}$ is any basis set and $\{w_i\}$ are some weights with $w_i \geq 0$ that sum to one, a density matrix would look like

$$\hat{\rho} = \sum_i |\varphi_i\rangle \, w_i \, \langle \varphi_i|. \tag{10}$$

In the Schrödinger representation, we calculate

$$i\hbar \frac{d}{dt} \left\langle \psi(t)|\hat{Q}|\psi(t)\right\rangle = \left\langle \psi(t)|[\hat{Q},\hat{H}]|\psi(t)\right\rangle$$

and identify

$$i\hbar\dot{\hat{Q}} = [\hat{Q}, \hat{H}]$$

The same logic applied to (10) gives

$$i\hbar\frac{d}{dt}\hat{\rho} = [\hat{H}, \hat{\rho}] = -[\hat{\rho}, \hat{H}] \tag{11}$$

Thus we identify

$$\begin{aligned} \hat{Q}(t) =& e^{i\hat{H}t/\hbar}\hat{Q}e^{-i\hat{H}t/\hbar}, \\ \hat{\rho}(t) =& e^{-i\hat{H}t/\hbar}\hat{\rho}e^{i\hat{H}t/\hbar}, \\ Q(t) =& \mathrm{Tr}[\hat{\rho}(t)\hat{Q}] = \mathrm{Tr}[\hat{\rho}(0)\hat{Q}(t)]. \end{aligned} \tag{12}$$

A density matrix will only be time independent if it commutes with the Hamiltonian. That is, the density matrix for an equilibrium system can only depend upon "constants of the motion." Of course (8) has this form.

There is an important subset of the set of possible density matrices, those for which

$$\hat{\rho}^2 = \hat{\rho}.$$

For these density matrices, the eigenvalues satisfy $\lambda^2 = \lambda$, whence they are 0 or 1. In the basis set that diagonalizes $\hat{\rho}$, the diagonal matrix elements will be 0 or 1, but only one can be 1 since (9) must be satisfied. If ϕ is the eigenvector with eigenvalue 1, then

$$\hat{\rho} = |\phi\rangle\langle\phi|$$

and

$$\langle Q\rangle = \mathrm{Tr}[\hat{\rho}\hat{Q}] = \langle\phi|\hat{Q}|\phi\rangle.$$

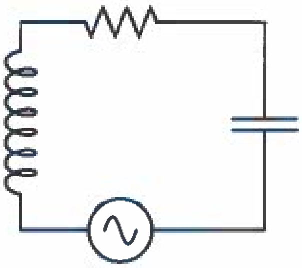
This is the degenerate case where the"statistical ensemble" only contains one state. Only in this special case can the matter be characterized by a wave function ϕ.

2. *A critique*

This is the mathematical apparatus presented in an introductory statistical mechanical course. But it is as mysterious as is the application of Fermi's golden rule to DGS's decay problem. Why aren't there any Q_{ij} terms with $i \neq j$ in (5)? Wouldn't (5) only apply if we made an ensemble of measurements of the energy followed by measurements of $\hat{Q}$, averaging the $\hat{Q}$ results? If $Q(t)$ is real, $Q(t) = Q(-t)$. Then how can (10) lead to an irreversible relaxation of any initial $\hat{\rho}(t) \rightarrow$ the equilibrium form (8)?

C. A Second Look at the Measurement Problem

1. *A Simple NMR Experiment*



Let me idealize the NMR experiment in this way. A magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\boldsymbol{B}$ will precess around the magnetic field vector. If there is an electric coil near $\boldsymbol{\mu}$, the magnetic flux through the coil will change as $\boldsymbol{\mu}$ precesses, inducing an $\mathcal{EMF}$ in the coil that can be observed. Hence, to measure the magnetic moment of a proton, we place the proton in a field aligned in the z-direction, $\boldsymbol{B} = B_0\,\hat{\boldsymbol{k}}$, at the center of a coil with symmetry axis aligned in the x-direction. To enhance the response, we connect the coil to a capacitor to create a resonant circuit with frequency equal to the precessional frequency of the proton.

The equivalent circuit for this is shown in the Figure. The AC signal generated in the coil is

$$v_{coil}(t) \propto \dot{\mu}_x(t)$$

and this leads to a voltage across the capacitor

$$v_{signal}(t) = \frac{\sqrt{LC}}{RC}\,v_{coil}(t)$$

This voltage is coupled to a transistor $\cdots$.

2. *Where is a Measurement Made?*

The output of the spectrometer is a *classical* signal, but the magnetic moment of the proton,

$$\boldsymbol{\mu} = \gamma\hbar\hat{\boldsymbol{s}}, \quad \text{with } \hat{s}_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \hat{s}_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \ \hat{s}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix},$$

is a quantum mechanical operator. We start by describing the proton with a spinor wavefunction ϕ. The state evolves in time under the influence of the Hamiltonian

$$\hat{H} = -\gamma\hat{s}_z\hbar B_0 = -2\,\hbar\,\omega\,\hat{s}_z \tag{1}$$

giving

$$\phi(t) = e^{-i\hat{H}t/\hbar}\phi(0) = e^{2\,i\,\omega\,t\,\hat{s}_z}\phi(0) = \begin{bmatrix} e^{i\,\omega\,t} & 0 \\ 0 & e^{-i\,\omega\,t} \end{bmatrix}\phi(0). \tag{2}$$

The expectation of μ_x is γ times

$$\langle\hat{s}_x\rangle = \langle\phi\,|s_x|\,\phi\rangle\,\cos(\omega\,t) + \left\langle\phi\,\middle|s_y\middle|\,\phi\right\rangle\,\sin(\omega\,t). \tag{3}$$

A "quantum measurement" is made somewhere between (2) and the output of the spectrometer.

3. *The Measurement*

At an elementary particle level, the interaction between the spin of the proton and the detection coil is an interaction between the spin of the proton and the charge of the electrons in the coil. Both the proton and the electrons are traditionally viewed as quantum objects. The coil, however, presents two special features.

1° There are many electrons in the coil. While each electron has a large quantum uncertainty about where it is (i.e., about it's contribution to the charge on the capacitor), the capacitor sees the sum of the contributions of many electrons. If a quantum mechanical uncertainty σ is associated with each electron, the uncertainty associated with N electrons will be $\sigma/\sqrt{N}$ if each electron makes a statistically independent contribution.

2° The electrons, however, will only make statistically independent contributions to the observed voltage if the motion of the electrons in the coil are uncorrelated. Since the *same* driving field is applied to *all* the electrons (there is just one proton), the motion in the electrons induced by the precession of the proton should be completely correlated.

The second feature of the coil, however, is its *resistance*. The electrons in the coil are coupled to a *heat bath*. While the proton is trying to correlate the motion of these electrons, the heat bath is trying to destroy any correlation between the electrons. The proton induced correlation in the electrons is transported into the heat bath, leaving no visible correlation in the electrons.

We are accustomed to ignoring the quantum uncertainty associated with the states of macroscopic systems. To get a rough image of how this comes about, suppose the electrons in the coil do not interact and ignore the fact that they are Fermions. If the interaction with the heat bath is ignored, each electron's state will propagate in time according to

$$\phi(t) = e^{-\frac{i}{\hbar}\int_0^t d\tau \hat{H}(\tau)} \phi(0)$$

with $\hat{H}(t)$ characterizing the spin dynamics of the sample. The effect of the interaction with the heat bath will be small erratic changes in the energy of the electron and hence the accumulation of an additional, stochastic phase shift, i.e.,

$$\phi(t) = e^{-\frac{i}{\hbar}\int_0^t d\tau \left[\hat{H}(\tau) + \xi(\tau)\right]} \phi(0).$$

To characterize $\xi(\tau)$ precisely, we'd have to solve the equations of motion for the heat bath. $\xi(\tau)$ should be an operator, but I will take it to be a scalar with ensemble average properties

$$\begin{aligned}
\overline{\xi(t)} &= 0,\\
\overline{\xi(t_1)\,\xi(t_2)} &= A\,\delta(t_2-t_1),\\
\overline{\xi(t_1)\,\xi(t_2)\,\xi(t_3)} &= 0,\\
\overline{\xi(t_1)\,\xi(t_2)\,\xi(t_3)\,\xi(t_4)} &= \\
&\quad A^2[\delta(t_2-t_1)\,\delta(t_4-t_3)+\delta(t_3-t_1)\,\delta(t_4-t_2)+\delta(t_4-t_1)\,\delta(t_2-t_3)],\\
&\quad\ldots
\end{aligned}$$

The amplitude A of the fluctuations is $\propto \hbar\, k_B T$.

The integral $\int\limits_0^t d\tau\,\xi(\tau)$ accumulates a stochastic phase shift that grows in time. To estimate the memory time of the wave function, we would ensemble average the time auto-correlation function

$$\phi(t_2)\cdot\phi(t_1)^* = F(t_2,t_1)\,e^{-\frac{i}{\hbar}\int\limits_{t_1}^{t_2} d\tau\,\xi(\tau)}\,.$$

$F(t_2,t_1)$ describes the bath-free dynamics. The ensemble average of the exponential factor gives

$$\overline{e^{-i\int\limits_{t_1}^{t_2} d\tau\,\xi(\tau)/\hbar}} = e^{-A\,|t_2-t_1|/2\hbar^2}\,.$$

The memory decays in time with a rate that is proportional to the coupling to the heat bath. The coupling to the heat bath makes the wave function forget its past.

Since each electron in the coil has a different interaction with the heat bath, the heat bath destroys the coherence between the electrons. Thus the actual character of the electrons is a steady state between the rise of coherence associated with deterministic dynamical motion (the equation of motion for a wave function has a *diffusive* form) and the destruction of coherence due to the coupling with the heat bath.

4. *The Conclusion*

Where does something get "squared?" There is no squaring. It is the natural motion of the electrons in the coil that leads to a signal that follows the rules of classical dynamics.

My argument for this is *heuristic*. Can I give a more formal argument? The answer is "yes and no." The description of the measurement is no different than the description of the time evolution of DGS's system or the relaxation to thermodynamic equilibrium of any system. We have a general formalism for this. But the formalism hides an essential uncertainty: Will the system actually exhibit irreversible behavior? In general, we know the answer empirically. But we have no abstract measure of Hamiltonians that predicts how a system will behave.

D. Subsystem Properties

1. *System* $\oplus$ *Field*

Let me shift notation. Suppose *system* refers to mechanical system that is the focus of attention. This has coordinates $\{q_i\}$ and a Hamiltonian $\hat{H}_{sys}$. But this system is connected to other coordinates, $\{Q_I\}$ that will be vaguely referred to as the "field". The field alone would have a Hamiltonian $\hat{H}_{field}$, and the Hamiltonian that governs the composite system + field is

$$\hat{H} = \hat{H}_{sys} + \hat{H}_{field} + \hat{V}.$$

$\hat{H}_{sys}$ operates in the space with coordinates $\{q_i\}$, $\hat{H}_{field}$ operates in the space with coordinates $\{Q_I\}$, but $\hat{V}$, the coupling between these two parts, involves both these sets of coordinates. If $\{\psi(q)_i\}$ form a basis set for states of the system and $\{\Phi(Q)_I\}$ form a basis set for states of the field, the functions $\{\psi_i\,\Phi_I\}$ will be a basis set for the composite system. Any state $\Psi(t)$ can be represented

$$\Psi(t) = \sum_{i,I} C_{iI}(t)\,\psi_i\,\Phi_I \tag{1}$$

Suppose that we want to observe a system property $\hat{Q}$.

$$\begin{aligned}
\langle Q\rangle =&\langle\Psi(t)|Q|\Psi(t)\rangle\\
=&\Big\langle\sum_{i,I} C_{iI}(t)\,\psi_i\,\Phi_I\Big|Q\Big|\sum_{j,J} C_{jJ}(t)\,\psi_j\,\Phi_J\Big\rangle\\
=&\sum_{i,j,I,J} C_{iI}(t)^*\,C_{jJ}(t)\big\langle\psi_i\,\Phi_I\big|Q\big|\psi_j\,\Phi_J\big\rangle\\
=&\sum_{i,j,I,J} C_{iI}(t)^*\,C_{jJ}(t)\big\langle\psi_i|Q|\psi_j\big\rangle\langle\Phi_I|\Phi_J\rangle\\
=&\sum_{i,j,I} C_{iI}(t)^*\,C_{jI}(t)\,Q_{ij}\\
=&\sum_{i,j} Q_{ij}\,\sum_I C_{iI}(t)^*\,C_{jI}(t)
\end{aligned}$$

Now *define* a density matrix for the system by giving it's matrix elements

$$\hat{\rho}_{ji}(t) = \sum_I C_{iI}(t)^*\,C_{jI}(t) \tag{2}$$

Then

$$\langle Q(t)\rangle = \mathrm{Tr}[\hat{Q}\,\hat{\rho}(t)] = \mathrm{Tr}[\hat{\rho}(t)\,\hat{Q}]$$

In Dirac notation, (2) is

$$\hat{\rho} = \sum_I \langle\Phi_I|\Psi(t)\rangle\,\langle\Psi(t)|\Phi_I\rangle \tag{3}$$

L. D. Landau's view was that there was no system that was "isolated" from the rest of the universe. Thus no system had a *wave function*. But every system has a density matrix.

E. van Hove's Formulation

1. *Ingredients*

In two papers (1955, 1956) L. van Hove gave a general quantum mechanical formulation of the "first order relaxation" problem. The formulation could describe the approach of a system to equilibrium or the radiative decay of a system. This was followed immediately by classical mechanical descriptions of the relaxation of a system to equilibrium coming out of I. Prigogine's "Brussels Group." R. Zwanzig reformulated both arguments to (1) clarify what the essential ingredients of the arguments were and (2) show that the structures of both approaches were the same.

The essential ingredients are

- the application of second order perturbation theory. The coupling between the matter and field are, after all, weak. But the analysis is not limited to short times.
- calculation of a density matrix. This postpones the "squaring" issue.
- the recognition that the system has a high density of states. These are described "statistically," rather than explicitly.
- that a particular observable is the target. This means there is a particular basis set in which the problem is formulated.

2. *What do we seek?*

As spectroscopists or thermodynamicists, we'd like to describe the system with something like

$$\frac{d\,p_n(t)}{dt} = \sum_{m>n} k_{nm}\,p_m(t) - p_n(t)\sum_{m<n} k_{nm}, \tag{A.1}$$

with the $p_n(t)$ the probabilities that a system will appear to be various energy eigenstates at time t.

Almost. The "energy eigenstates" are associated with a Hamiltonian that is not the real Hamiltonian of the system. The spectroscopist imagines states of a system that does not interact with the electromagnetic field, the thermodynamicist imagines states of a system that does not interact with a heat bath. This skewed view explains why there *is* time evolution. Otherwise $dp_n(t)/dt = 0$ for all n. The rate constants in (A.1) come from photon-matter coupling or state-heat bath coupling.

Let $\hat{H}_0$ represent the Hamiltonian whose eigenstates are the states that the $p_n(t)$ are supposed to describe. If we use these eigenstates as a basis set, then

$$\rho_{nn}(t) = p_n(t).$$

So Eq.(A.1) asserts that, in this representation, the time evolution of the diagonal elements of the density matrix is determined completely by the diagonal elements themselves.

If the actual time evolution is induced by $\hat{H}_0 + \hat{V}$, it is easy (and simpler) to require that $\hat{V}$ have *no diagonal matrix element*: Simply add any diagonal terms to $\hat{H}_0$.

3. *Super Operators*

Quantum mechanics constructs operators that operate on state vectors. The state vectors form a vector space. That is, state vectors can be combined to form new state vectors,

$$\{\alpha, \psi, \beta, \phi\} \to \alpha * \psi + \beta * \phi.$$

But the operators themselves can be similarly combined. They form their own vector space. We will call operators that operate on this vector space of operators *super operators*. There are two super operators whose introduction simplifies an otherwise complex notation.

The actual equation of motion of $\hat{\rho}(t)$,

$$i\hbar \frac{d}{dt}\hat{\rho} = [\hat{H}_0 + \hat{V}, \hat{\rho}], \tag{1}$$

says that $d\hat{\rho}/dt$ is linearly related to $\hat{\rho}$. Define the *Liouville operator* $\mathcal{L}$ (a super operator) by

$$\frac{d\hat{\rho}(t)}{dt} = -\mathcal{L}\,\hat{\rho}(t) = -\mathcal{L}_0\hat{\rho}(t) - \mathcal{L}_V\hat{\rho}(t).$$

$\mathcal{L}_V\,\hat{A}$, for example, maps an operator $\hat{A}$ into a new operator,

$$\mathcal{L}_V\,\hat{A} = \frac{i}{\hbar}[\hat{V}, \hat{A}].$$

The second super operator $\mathcal{P}$ projects out the off-diagonal parts of an operator. In the basis set defined by $\hat{H}_0$,

$$\left[\mathcal{P}\hat{A}\right]_{mn} = \hat{A}_{nn}\,\delta_{mn}$$

$\mathcal{P}\hat{A}$ is "diagonal." $\mathcal{P}^2 = \mathcal{P}$, a property of all *projection* operators. Using $\mathcal{P}$, we can separate the diagonal and off-diagonal components of $\hat{\rho}$.

$$\hat{\rho}_d = \mathcal{P}\,\hat{\rho}, \qquad \hat{\rho}_{od} = (1-\mathcal{P})\hat{\rho}.$$

With this separation, (1) gives two, coupled dynamical equations,

$$\frac{d\hat{\rho}_d}{dt} = -\,\mathcal{P}\mathcal{L}\,\hat{\rho}_d - \mathcal{P}\mathcal{L}\,\hat{\rho}_{od} \tag{2}$$

$$\frac{d\hat{\rho}_{od}}{dt} = -\,(1-\mathcal{P})\mathcal{L}\,\hat{\rho}_d - (1-\mathcal{P})\mathcal{L}\,\hat{\rho}_{od} \tag{3}$$

Now

$$\begin{aligned}\mathcal{P}\mathcal{L}\,\hat{\rho}_d &= \frac{i}{\hbar}\mathcal{P}[\hat{H}_0 + \hat{V}\,,\hat{\rho}_d] \\ &= \frac{i}{\hbar}\mathcal{P}[\hat{V}\,,\hat{\rho}_d] = 0\end{aligned}$$

because $[\hat{H}_0, \hat{\rho}_d] = 0$, while

$$\begin{aligned}\mathcal{P}\mathcal{L}\,\hat{\rho}_{od} &= \frac{i}{\hbar}\mathcal{P}[\hat{H}_0 + \hat{V}\,,\hat{\rho}_{od}] \\ &= \frac{i}{\hbar}\mathcal{P}[\hat{V}\,,\hat{\rho}_{od}] = \mathcal{P}\mathcal{L}_V\,\hat{\rho}_{od}\end{aligned}$$

so (2) can be written

$$\frac{d\hat{\rho}_d}{dt} = -\mathcal{P}\mathcal{L}_V\,\hat{\rho}_{od}. \tag{4}$$

The rate of change of the diagonal elements of the density matrix is actually determined by the off-diagonal matrix elements!

The "random phase approximation" suggests that $\hat{\rho}$ will start diagonal. Anyway, suppose that $\hat{\rho}_{od}(0) = 0$. Including other initial conditions is straight-forward, but I don't know of any interesting applications with other initial conditions. With this initial condition, the Laplace transform of (3) is

$$s\,\tilde{\rho}_{od}(s) = -(1-\mathcal{P})\mathcal{L}\,\tilde{\rho}_d(s) - (1-\mathcal{P})\mathcal{L}\,\tilde{\rho}_{od}(s) \tag{5}$$

which can be iterated to generate

$$\tilde{\rho}_{od}(s) = \left\{\sum_{k=1}^{n}\left[-\frac{1}{s}(1-\mathcal{P})\mathcal{L}\right]^k\right\}\tilde{\rho}_d(s) + \left[-\frac{1}{s}(1-\mathcal{P})\mathcal{L}\right]^n\tilde{\rho}_{od}(s)$$

or

$$\hat{\rho}_{od}(t) = -\int_0^t d\tau (1-\mathcal{P})\mathcal{L} \sum_{k=0}^{n-1} \frac{(-\tau)^k}{k!} \left[(1-\mathcal{P})\mathcal{L}\right]^k \hat{\rho}_d(t-\tau)$$
$$-\int_0^t d\tau (1-\mathcal{P})\mathcal{L} \frac{(-\tau)^n}{n!} \left[(1-\mathcal{P})\mathcal{L}\right]^n \hat{\rho}_{od}(t-\tau)$$

Taking $n \to \infty$ gives

$$\begin{aligned}\hat{\rho}_{od}(t) &= -\int_0^t d\tau e^{-(1-\mathcal{P})\mathcal{L}\tau} (1-\mathcal{P})\mathcal{L}\, \hat{\rho}_d(t-\tau) \\ &= -\int_0^t d\tau e^{-(1-\mathcal{P})\mathcal{L}\tau} (1-\mathcal{P})\mathcal{L}_V\, \hat{\rho}_d(t-\tau) \qquad (6)\end{aligned}$$

showing how the off-diagonal terms are determined by the diagonal terms.

Using (6) to eliminate $\hat{\rho}_{od}(t)$ in (4) gives an equation for the diagonal terms alone,

$$\frac{d\hat{\rho}_d(t)}{dt} = \mathcal{P}\mathcal{L}_V \int_0^t d\tau e^{-(1-\mathcal{P})\mathcal{L}\tau} (1-\mathcal{P})\mathcal{L}_V\, \hat{\rho}_d(t-\tau). \qquad (7)$$

Equation (7) is exact, but complicated. To simplify this result, first note that there are two explicit $\hat{V}$ factors. So the second order perturbative result is obtained by removing all *other* $\hat{V}$ factors. To second order in $\hat{V}$,

$$\frac{d\hat{\rho}_d(t)}{dt} \approx \mathcal{P}\mathcal{L}_V \int_0^t d\tau e^{-(1-\mathcal{P})\mathcal{L}_0\tau} (1-\mathcal{P})\mathcal{L}_V\, \hat{\rho}_d(t-\tau). \qquad (8)$$

To evaluate this expression, start with

$$[\mathcal{L}_V\, \hat{\rho}_d]_{mn} = \frac{i}{\hbar} V_{mn}(\rho_{nn} - \rho_{mm}).$$

This is off-diagonal, so the subsequent $(1-\mathcal{P})$ factor in (8) has no influence. If $\hat{Z}$ represents this result,

$$\begin{aligned}\left[e^{-(1-\mathcal{P})\mathcal{L}_0\tau}\hat{Z}\right]_{mn} &= \left\{1 - \frac{i\tau}{\hbar}(E_m - E_n) + \frac{1}{2}\left(-\frac{i\tau}{\hbar}\right)^2 (E_m - E_n)^2 + \cdots\right\} Z_{mn} \\ &= e^{-i(E_m - E_n)\tau/\hbar}\, Z_{mn}\end{aligned}$$

whence

$$\frac{d\rho_{nn}(t)}{dt} = -\frac{2}{\hbar^2}\int_0^t d\tau \sum_k |V_{nk}|^2 \cos\left[\frac{(E_n - E_k)\,\tau}{\hbar}\right][\rho_{nn}(t-\tau) - \rho_{kk}(t-\tau)] \qquad (9)$$

This has the qualitative form of (A.1), but it shows that the system has *memory*: The time evolution of $\rho_{nn}(t)$ is determined by the previous *histories* of the diagonal matrix elements. If we define

$$K_{nn,kk}(\tau) = \frac{2}{\hbar^2}\,|V_{nk}|^2 \cos\left[\frac{(E_n - E_k)\,\tau}{\hbar}\right] \qquad (11)$$

then

$$\frac{d\rho_{nn}(t)}{dt} = -\int_0^t d\tau \sum_k K_{nn,kk}(\tau)\,[\rho_{nn}(t-\tau) - \rho_{kk}(t-\tau)] \qquad (12)$$

$K_{nn,kk}(\tau)$ is a memory function that explains how the memory of the *phases* of the density matrix elements influences time evolution of the system. The details of the time evolution depend upon the characteristic properties of the system. As a general rule, the $K_{nn,kk}(\tau)$ will decay → 0 as τ grows. The system will have a finite *memory time*.

F. Fermi's Golden Rule

Equation (E.12) exhibits memory. The time evolution is not the Markov process assumed in (A.1). What the difference is depends upon the details of the system, the distribution of states and the magnitude of the $|V_{nk}|^2$.

The Markovian approximation will be excellent, however, if

$$\rho_{nn}(t-\tau) - \rho_{kk}(t-\tau) \approx \rho_{nn}(t) - \rho_{kk}(t),$$

if the change in the diagonal components is small on the time scale of the memory of $K_{nn,kk}(\tau)$. Since the rate of change of the diagonal components of the density matrix is $\mathcal{O}\left(|V_{nk}|^2\right)$, this condition will be satisfied for sufficiently small $|V_{nk}|^2$. Thus, if we look at a system with sufficiently small $|V_{nk}|^2$ at times $t \gg$ the memory time of $K_{nn,kk}(\tau)$, (E.12) reduces to

$$\frac{d\rho_{nn}(t)}{dt} = -\sum_k K_{nn,kk}\,[\rho_{nn}(t) - \rho_{kk}(t)] \qquad (1)$$

with the rate constants

$$K_{nn,kk} = \frac{2}{\hbar^2}\,|V_{nk}|^2 \int_0^\infty d\tau \cos\left[\frac{(E_n - E_k)\,\tau}{\hbar}\right] = \frac{2\pi}{\hbar}\,|V_{nk}|^2\,\delta(E_n - E_k).$$

If we say that $|V_{nk}|^2$ doesn't vary with final field state and we sum over all final field states, $\delta(E_n - E_k) \rightarrow \mathcal{D}(\mathcal{E}_{field})$, the density of states in the field. In this case Fermi's Golden Rule for the rate constants is recovered.

The short time approximation of the naive analysis has been replaced by the approximation that time evolution is slow on the observation time scale. In fact, van Hove described (1) as being the first approximation in

$$\lambda = |V_{nk}|^2 \cdot t.$$

It always fails at sufficiently long times, but how long depends upon the magnitude of $|V_{nk}|^2$. If $|V_{nk}|^2$ isn't that small, or we want to describe the dynamics over a longer time, we must go back to (E.7) and make a better approximation.

G. Examples of Magnetic Resonance Usage

1. *A Single Spin*

Consider of a single, unpaired electron on a molecule in a liquid phase. If $\vec{s}$ is the vector with $\hbar\times$ Pauli spin matrices for components, the electron's magnetic moment operator will be

$$\vec{\mu} = -\gamma\vec{s}$$

The motion of the magnetic moment in a magnetic field $\vec{B}$ will be determined by the Hamiltonian

$$H = -\vec{\mu}\cdot\vec{B}.$$

Consider this experiment. The spin is initially oriented along the x-axis (spin state α_x) and the magnetic field is

$$\vec{B}(t) = B_0\hat{z} + \boldsymbol{b}(t)$$

with $B_0\hat{z}$ a large external field oriented along the z-axis and $\boldsymbol{b}(t)$ a much smaller field arising from the interaction with the magnetic moments of the nuclei in the system. $\boldsymbol{b}(t)$ fluctuates in time. By symmetry, $\langle b_x(t)\rangle = \left\langle b_y(t)\right\rangle = 0$. We can make $\langle b_z(t)\rangle = 0$ by redefining B_0. A detection wire coiled around the electron allows us to observe $\mu_x(t)$.

If we represent matrices in the α_z, β_z basis set,

$$\hat{\rho}(0) = |\alpha_x\rangle\langle\alpha_x| = \frac{1}{2}\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \tag{1}$$

and

$$\hat{H} = \begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} \hbar\omega & 0 \\ 0 & -\hbar\omega \end{bmatrix} - \frac{1}{2}\gamma\hbar\begin{bmatrix} b_z(t) & b_-(t) \\ b_+(t) & -b_z(t) \end{bmatrix} \tag{2}$$

with $\omega = \gamma B_0$ and $b_\pm(t) = b_x(t) \pm i b_y(t)$. Note that $h_{22} = -h_{11}$ and $h_{21} = h_{12}^*$.

In time, $\hat{\rho}(0)$ propagates via the rule

$$i\hbar\frac{d}{dt}\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)] \tag{3}$$

and the signal observed is

$$S(t) = -\gamma\,\mathrm{Tr}[\hat{\rho}(t)\hat{s}_x] = -\frac{1}{2}\gamma\hbar\,\left[\rho_{12}(t) + \rho_{21}(t)\right]. \tag{4}$$

2. *Superoperator View*

The rate of change of $\rho(t)$ is fixed by

$$[\hat{H}, \hat{\rho}] = \begin{bmatrix} h_{12}\rho_{21} - h_{21}\rho_{12} & -(h_{22} - h_{11})\rho_{12} + h_{12}(\rho_{22} - \rho_{11}) \\ -h_{21}(\rho_{22} - \rho_{11}) + \rho_{21}(h_{22} - h_{11}) & -h_{12}\rho_{21} + h_{21}\rho_{12} \end{bmatrix}$$

Now shift from picturing $\hat{\rho}(t)$ as an operator on spin states to picturing this operator as a 4 component vector,

$$\vec{\rho}(t) = \begin{bmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{bmatrix}$$

Then the equations of motion for $\vec{\rho}(t)$ are

$$\frac{d}{dt}\,\vec{\rho}(t) = -\mathcal{L}\,\vec{\rho}(t) \tag{5}$$

with

$$\mathcal{L} = \frac{i}{\hbar}\begin{bmatrix} 0 & -h_{21} & h_{12} & 0 \\ -h_{12} & -h_{22}+h_{11} & 0 & h_{12} \\ h_{21} & 0 & h_{22}-h_{11} & -h_{21} \\ 0 & h_{21} & -h_{12} & 0 \end{bmatrix}$$

a *superoperator* in the sense of Zwanzig.

A perturbative solution will be developed, based on the fact that $|\boldsymbol{b}(t)| \ll B_0$. To this end, separate

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_V$$

with

$$\mathcal{L}_0 = i\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \omega & 0 & 0 \\ 0 & 0 & -\omega & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

and

$$\mathcal{L}_V = -\frac{i\,\gamma}{2}\begin{bmatrix} 0 & -b_+(t) & b_-(t) & 0 \\ -b_-(t) & 2b_z(t) & 0 & b_-(t) \\ b_+(t) & 0 & -2b_z(t) & -b_+(t) \\ 0 & b_+(t) & -b_-(t) & 0 \end{bmatrix}$$

Since $\mathcal{L}_0$ is independent of time, (5) is equivalent to

$$\vec{\rho}(t) = e^{-\mathcal{L}_0\,t}\,\vec{\rho}(0) - \int_0^t d\tau\, e^{-\mathcal{L}_0\,(t-\tau)}\,\mathcal{L}_V(\tau)\,\vec{\rho}(\tau)$$

Iterating this relation gives

$$\vec{\rho}(t) = \Big\{ e^{-\mathcal{L}_0\, t} - \int_0^t d\tau\, e^{-\mathcal{L}_0\,(t-\tau)}\, \mathcal{L}_V(\tau)\, e^{-\mathcal{L}_0\,\tau} + \int_0^t d\tau \int_0^\tau d\tau'\, e^{-\mathcal{L}_0\,(t-\tau)}\, \mathcal{L}_V(\tau)\, e^{-\mathcal{L}_0\,(\tau-\tau')}\, \mathcal{L}_V(\tau') e^{-\mathcal{L}_0\,\tau'} + \mathcal{O}\left(\mathcal{L}_V\right)^3 \Big\}\, \vec{\rho}(0)$$

If we average over the ensemble of $b(t)$ fields,

$$\langle \mathcal{L}_v \rangle = 0.$$

Thus, to second order in $b(t)$,

$$\langle \vec{\rho}(t) \rangle = \Big\{ e^{-\mathcal{L}_0\, t} + \int_0^t d\tau \int_0^\tau d\tau'\, e^{-\mathcal{L}_0\,(t-\tau)} \Big\langle \mathcal{L}_V(\tau)\, e^{-\mathcal{L}_0\,(\tau-\tau')}\, \mathcal{L}_V(\tau') \Big\rangle\, e^{-\mathcal{L}_0\,\tau'} \Big\}\, \vec{\rho}(0). \quad (6)$$

With

$$\vec{\rho}(0) = \frac{1}{2} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix},$$

(6) reduces to

$$\langle \vec{\rho}(t) \rangle = \frac{1}{2} \left\{ \begin{bmatrix} 1 \\ e^{-i\,\omega\, t} \\ e^{i\,\omega\, t} \\ 1 \end{bmatrix} + \int_0^t d\tau \int_0^\tau d\tau'\, e^{-\mathcal{L}_0\,(t-\tau)} \Big\langle \mathcal{L}_V(\tau)\, e^{-\mathcal{L}_0\,(\tau-\tau')}\, \mathcal{L}_V(\tau') \Big\rangle \begin{bmatrix} 1 \\ e^{-i\,\omega\,\tau'} \\ e^{i\,\omega\,\tau'} \\ 1 \end{bmatrix} \right\} \quad (7)$$

As the fluctuations in $b(t)$ are *stationary*, the terms in the ensemble average in (7) must be functions of $\tau - \tau'$. To get a concrete result, I will assume that $b_x(t), b_y(t)$ and $b_z(t)$ are all statistically independent and I will ignore the fluctuations in $b_z(t)$ (which are a little more complex because they involve a Boltzmann factor). Thus the only quantity assumed to be relevant is

$$\Big\langle b_x(\tau) b_x(\tau') \Big\rangle = \Big\langle b_y(\tau) b_y(\tau') \Big\rangle = \phi(\tau - \tau'),$$

the correlation function for fluctuations transverse to the B_0 field. With this approximation

$$\left\langle \mathcal{L}_V(\tau)\, e^{-\mathcal{L}_0(\tau-\tau')}\, \mathcal{L}_V(\tau') \right\rangle$$
$$= -\frac{\gamma^2}{2}\begin{bmatrix} 2\cos[\omega(\tau-\tau')] & 0 & 0 & -2\cos[\omega(\tau-\tau')] \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -2\cos[\omega(\tau-\tau')] & 0 & 0 & 2\cos[\omega(\tau-\tau')] \end{bmatrix} \phi(\tau-\tau')$$

whence

$$\langle \vec{\rho}(t)\rangle = \frac{1}{2}\left\{ \begin{bmatrix} 1 \\ e^{-i\omega t} \\ e^{i\omega t} \\ 1 \end{bmatrix} - \frac{\gamma^2}{2}\int_0^t d\tau \int_0^\tau d\tau'\, \phi(\tau-\tau') \begin{bmatrix} 0 \\ e^{-i\omega(t-\tau+\tau')} \\ e^{i\omega(t-\tau+\tau')} \\ 0 \end{bmatrix} \right\}$$

In particular,

$$\langle \rho_{12}(t)\rangle = \frac{1}{2}\left\{ e^{-i\omega t} - \frac{\gamma^2}{2}\int_0^t d\tau \int_0^\tau d\tau'\, e^{-i\omega(t-\tau+\tau')}\, \phi(\tau-\tau') \right\}$$

To second order in $b(t)$, this is equivalent to

$$\langle \rho_{12}(t)\rangle = \frac{1}{2}\exp\left\{ -i\omega t - \frac{\gamma^2}{2}\int_0^t d\tau \int_0^\tau d\tau'\, e^{i\omega\tau'}\, \phi(\tau') \right\}$$

[Compare with the equation on the bottom of page 7.]

For $t >$ the memory time of the transverse fluctuations,

$$\frac{\gamma^2}{2}\int_0^t d\tau \int_0^\tau d\tau'\, e^{i\omega\tau'}\, \phi(\tau') = \frac{\gamma^2 t}{2}\int_0^\infty d\tau'\, e^{i\omega\tau'}\, \phi(\tau') = (\Gamma + i\,\Omega)\, t$$

and

$$\langle \rho_{12}(t)\rangle = \frac{1}{2}\exp\{-i\omega t - (\Gamma + i\,\Omega)\, t\} = \frac{1}{2}\exp\{-i\,(\omega+\Omega)\, t - \Gamma\, t\}$$

Recalling $\rho_{12} = \rho_{21}^*$, the observed signal is predicted to be

$$S(t) = -\frac{1}{2}\gamma\hbar\,[\rho_{12}(t) + \rho_{21}(t)] = -\frac{1}{2}\gamma\hbar\,\cos[(\omega+\Omega)\, t]\, e^{-\Gamma t}. \tag{8}$$

Γ^{-1} would be the "T_2" for the system. Neglecting the fluctuations in $b_z(t)$ makes this the only source of linewidth in the signal.

3. *Chemical Exchange*

The signal (F.8) is Fourier transformed to obtain what would have been seen in a "continuous wave" spectrometer. That is, the *spectrum* of the electron would be

$$I(\nu) = C\frac{\Gamma}{(\nu - \omega - \Omega)^2 + \Gamma^2}$$

If the electron could be on two distinct molecules with two distinct chemical shifts (Ω's) and linewidths (Γ's), then the reported signal would be

$$I(\nu) = C_1\frac{\Gamma_1}{(\nu - \omega - \Omega_1)^2 + \Gamma_1^2} + C_2\frac{\Gamma_2}{(\nu - \omega - \Omega_2)^2 + \Gamma_2^2} \tag{1}$$

The spectrum (1) would be seen if the electron did not jump between different molecules in the lifetime of the experiment. If the molecule jumped (if there was "chemical exchange"), the dynamics of $\mu_x(t)$ could be significantly altered. In the rapid exchange limit, one would expect the two Lorentzian lines in (1) to collapse into a single line.

To provide a dynamical model for this process, first simplify the results of §F.2 by saying that the equation of motion for an electron on a single site is

$$\frac{d}{dt}\vec{\rho}(t) = -\mathcal{L}\vec{\rho}(t)$$

with

$$\mathcal{L} = i\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \omega + \Omega + i\Gamma & 0 & 0 \\ 0 & 0 & -(\omega + \Omega + i\Gamma) & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

a time independent superoperator.

Each of the two classes of molecules provides a different dynamical environment for the electron. At any moment, however, the electron is in one or the other environment, so we could separately determine the density matrices that characterize the two environments. Let these be $\vec{\rho}_a$ and $\vec{\rho}_b$ If we interpret these as the *average* values of the density matrices, the equations of motion for these two quantities can be constructed in analogy with (A.1),

$$\begin{aligned} \frac{d}{dt}\vec{\rho}_a(t) &= -\mathcal{L}_a\vec{\rho}_a(t) - k\,\vec{\rho}_a(t) + k\,\vec{\rho}_b(t) \\ \frac{d}{dt}\vec{\rho}_b(t) &= -\mathcal{L}_b\vec{\rho}_b(t) - k\,\vec{\rho}_b(t) + k\,\vec{\rho}_a(t) \end{aligned} \tag{2}$$

with k the rate at which the electron hops from one environment to the other, the chemical exchange rate. [For simplicity, I've assumed that both environments are equally populated at equilibrium.]

If I further assume that both environments have the same T_2, (2) gives these equations of motion for the ρ_{12} components,

$$\begin{aligned}\frac{d}{dt}\rho_{a,12}(t) &= -[i(\omega+\Omega_a)+\Gamma]\,\rho_{a,12}(t) - k\,\rho_{a,12}(t) + k\,\rho_{b,12}(t)\\ \frac{d}{dt}\rho_{b,12}(t) &= -[i(\omega+\Omega_b)+\Gamma]\,\rho_{b,12}(t) - k\,\rho_{b,12}(t) + k\,\rho_{a,12}(t)\end{aligned} \tag{3}$$

Initially, $\rho_{a,12}(0)=\rho_{b,12}(0)=\frac{1}{2}$, so but the Laplace transform of (3) is

$$\begin{aligned}[s+k+\Gamma+i(\omega+\Omega_a)]\,\tilde{\rho}_{a,12}(s) - k\tilde{\rho}_{b,12}(s) &= \frac{1}{2}\\ -k\tilde{\rho}_{a,12}(s) + [s+k+\Gamma+i(\omega+\Omega_b)]\,\tilde{\rho}_{b,12}(s) &= \frac{1}{2}\end{aligned}$$

which fixes

$$\tilde{\rho}_{a,12}(s) = \frac{1}{2}\frac{s+2k+\Gamma+i(\omega+\Omega_b)}{[s+k+\Gamma+i(\omega+\Omega_a)][s+k+\Gamma+i(\omega+\Omega_b)]-k^2}$$

The general structure of the spectrum is determined by the poles of this function. There are two poles (so two Lorentzian lines) located at

$$s_\pm = -i(\omega+\frac{\Omega_a+\Omega_b}{2}) - k - \Gamma \pm \frac{1}{2}\sqrt{4k^2-(\Omega_a-\Omega_b)^2}$$

As k rises from 0 toward $|\Omega_a-\Omega_b|/2$, the two isolated lines begin to move toward each other and their width grows. When k passes $|\Omega_a-\Omega_b|/2$, there are two lines, both at the average frequency, but with widths that increase and decrease with increasing k. The narrower line is that which dominates the spectrum, of course. Thus, high exchange rates – or rapid phase shifting – can actually lead to sharper lines!