Statistical Mechanics of Irreversibility

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LECTURE I

Part 1

The purpose of these lectures is to describe and explain some mathematical techniques that are useful in quantum statistical mechanics. These techniques, not yet very well known, are connected with the use of Liouville operators and projection operators. Their main illustration here will be in the derivation of certain "master equations" of interest in the theory of irreversible processes.

First, a quick survey of some background material will be useful. This is connected with the following question.

The density matrix (operator) at time t is $\hat{\rho}(t)$. Its evolution is determined by the Hamiltonian operator

$$\hat{H} = H_0 + \lambda \hat{V}. \tag{1}$$

where $\hat{H}_0$ is some unperturbed Hamiltonian and $\lambda\hat{V}$ is a perturbation. The strength of the perturbation is measured by λ.

The unperturbed system $\hat{H}_0$ may consist of non-interacting particles, quasi-particles, etc.; it should have the property that we can find its eigenvalues and eigenstates,

$$\hat{H}_0|n\rangle = E_n|n\rangle \tag{2}$$

We shall work in this unperturbed representation. The density matrix is

$$\rho_{mn}(t) = \langle m|\hat{\rho}(t)|n\rangle \tag{3}$$

and the Hamiltonian is

$$H_{mn} = E_m \delta_{mn} + \lambda V_{mn} \tag{4}$$

For simplicity we assume that E_m contains all diagonal contributions, so that

$$V_{mm} = 0 \tag{5}$$

The diagonal elements of $\hat{\rho}$ describe the occupation of unperturbed states,

$\rho_{mm}(t)$ = prob. of observing the system in state $|m\rangle$ at time t. (6)

In the absence of a perturbation, $\rho_{mm}(t)$ is constant. This can be seen from the equation of motion,

$$\frac{\partial \hat{\rho}}{\partial t} = -i[\hat{H}, \hat{\rho}] \tag{7}$$

$$\frac{\partial \rho_{mn}}{\partial t} = -i \sum_l (H_{ml}\rho_{ln} - \rho_{ml} H_{ln})$$

and, for the diagonal elements, on putting in $E_m \delta_{mn} + \lambda V_{mn}$,

$$\frac{\partial \rho_{mm}}{\partial t} = -i \sum_l (\lambda V_{ml} \rho_{lm} - \rho_{ml} \lambda V_{lm}) \tag{8}$$

So if no perturbation, ρ_{mm} is constant in time.

With this long prelude, we can now state the problem of interest: What is the time dependence of the occupation probability $\rho_{mm}(t)$ as a result of the perturbation λV_{mn} ?

It turns out that there are at least two solutions to this problem. The first one is obtained from the Liouville equation just written,

$$\frac{\partial \hat{\rho}}{\partial t} = -i[\hat{H}, \hat{\rho}] \tag{9}$$

The formal solution to this equation is as follows,

$$\hat{\rho}(t) = e^{-it\hat{H}} \hat{\rho}(0)\ e^{+it\hat{H}} \tag{10}$$

so that

$$\rho_{mm}(t) = \sum_j \sum_k (e^{-itH})_{mj} \rho_{jk}(0) (e^{+it\hat{H}})_{km} \tag{11}$$

This determines in principle and exactly the desired time dependence, in terms of the initial values.

The most common special case is where the density matrix is initially diagonal,

$$\rho_{mn}(0) = \rho_{mm}(0) \delta_{mn} \tag{12}$$

Then

$$\rho_{mm}(t) = \sum_n \left| (e^{-itH})_{mn} \right|^2 \rho_{nn}(0) \tag{13}$$

so that

$$|(e^{-it\hat{H}})_{mn}|^2$$

gives the probability of transition from a state n at t = 0 to a state m at t.

We shall return to this solution in a little while. First we look at the other solution. This was given by Pauli:

$$\frac{\partial \rho_{mm}(t)}{\partial t} \cong \sum_n \left[W_{mn} \rho_{nn}(t) - W_{nm} \rho_{mm}(t) \right] \tag{14}$$

The coefficients W_{mn} are transition rates, given in the limit of weak interaction by the "Golden Rule,"

$$W_{mn} = 2\pi\lambda^2 |V_{mn}|^2 \delta(E_m - E_n) \tag{15}$$

ithout actually solving Pauli's master equation, we can ee that its solutions are not identical with the exact solutions. To do this we calculate the time derivatives at t = 0, with the special initial condition

$$\left\{ \begin{array}{l} \rho_{11}(0) = 1 \\ \text{all other } \rho_{mn}(0) = 0 \end{array} \right\} \tag{16}$$

Then the exact equation (8) is

$$\left(\frac{\partial \rho_{11}}{\partial t} \right)_0 = -i \sum_k \left[\lambda V_{1k} \rho_{1k}(0) - \lambda \rho_{1k}(0) V_{k1} \right] \tag{17}$$

But V_{1k} vanishes for k = 1 by the way we originally defined the perturbation, and $\rho_{1k}(0)$ vanishes for $k \neq 1$. Therefore the whole RHS vanishes, or

$$\left(\frac{\partial \rho_{11}}{\partial t}\right)_0 = 0 \tag{18}$$

But we can calculate this also from the master equation,

$$\left(\frac{\partial \rho_{11}}{\partial t}\right)_0 \cong \sum_n W_{1n}\,\rho_{nn}(0) - \sum_n W_{n1}\,\rho_{11}(0) \tag{19}$$

Note that W_{1n} vanishes for n = 1 and $\rho_{nn}(0)$ vanishes for $n \neq 1$. Therefore

$$\left(\frac{\partial \rho_{11}}{\partial t}\right)_0 \cong -\left(\sum_n W_{n1}\right)\rho_{11}(0) \tag{20}$$

The RHS cannot vanish because it contains a sum $\sum_n W_{n1}$ of intrinsically positive quantities. Se we have a contradiction.

In spite of this, the Pauli master equation is often nearly correct. We want to understand how this happens, and what the limitations are.

THE STANDARD DERIVATION

To begin with, let's look at the customary derivation of Pauli's equation. It takes the form of a gain-loss equation

$$\begin{aligned}\Delta\rho_{mm}(t) &= \text{net increase of occupation of state } |m\rangle \\ &\quad \text{during initial } \Delta t \\ &= \text{gain in } |m\rangle - \text{loss from } |m\rangle\end{aligned} \tag{21}$$

The gain can come only from other states. This is "obviously"

$$\begin{aligned}\text{gain in } |m\rangle &= \sum_n{}' \,[\text{prob. of transition from n to m during } \Delta t] \\ &\quad \times [\text{occupation of } |n\rangle] \\ &= \sum_n{}' \,[W_{mn}\,\Delta t]\; x\,\rho_{nn}(t)\end{aligned} \tag{22}$$

and the loss can come only from transitions to other states,

$$\text{loss from } |m\rangle = \left(\sum_n{}' W_{nm}\,\Delta t\right) \times \rho_{mm}(t) \tag{23}$$

Now we write

$$\frac{\partial \rho}{\partial t} = \frac{\Delta \rho}{\Delta t} \tag{24}$$

and we get the master equation. To conclude the derivation we must also get the "Golden Rule."

The derivation given by Schiff is typical of those in textbooks. It is based on first order perturbation theory. We start with Equation (15), where

$$\begin{aligned}|\,(e^{-it\hat{H}})_{mn}\,|^2 &= \text{prob. of transition from } |n\rangle \\ &\quad \text{initially to } |m\rangle \text{ at time t.}\end{aligned} \tag{25}$$

Use the perturbation expansion

$$\begin{aligned}e^{-it\hat{H}} &= e^{-it\hat{H}_0} - i\int_0^t dt_1\, e^{-i(t-t_1)\hat{H}_0}\,\lambda\hat{V}\,e^{-it_1\hat{H}_0} \\ &\quad \text{higher orders in } \lambda.\end{aligned} \tag{26}$$

As the general expansion theorem, note that

$$e^{-it\hat{H}} = e^{-it\hat{H}_0} - i\int_0^t dt_1\, e^{-i(t-t_1)\hat{H}_0}\,\lambda\hat{V}\,e^{-it_1\hat{H}} \tag{27}$$

This can be verified by differentiating. Eq. (26) is obtained by substituting

$$\exp(-it_1\hat{H}_0) \quad \text{for} \quad \exp(-it_1\hat{H}) \quad \text{on the RHS.}$$

Now we take the (m, n) matrix element and do the time integration. We restrict the discussion to transitions between different states, or $m \neq n$. Then

$$(e^{-it\hat{H}_0})_{mn} = e^{-itE_m}\delta_{mn} = 0 \tag{28}$$

and

$$\begin{aligned}(e^{-it\hat{H}})_{mn} &= i\int_0^t dt_1\; e^{-i(t-t_1)E_m}\,(\lambda V)_{mn}\,e^{-it_1E_n} \\ &= -\lambda V_{mn}\,\frac{e^{it\omega_{mn}}-1}{\omega_{mn}} \times e^{-itE_m}\end{aligned} \tag{29}$$

when

$$\omega_{mn} = E_m - E_n \tag{30}$$

We take the square; after some algebra, we get

$$|(e^{-it\hat{H}})_{mn}|^2 = 4\lambda^2 |V_{mn}|^2 \left[\frac{\sin^2 \frac{1}{2}\omega_{mn} t}{\omega_{mn}^2}\right] \tag{31}$$

Let's call the quantity in square brackets

$$\Delta(\omega, t) = \frac{\sin^2 \frac{1}{2}\omega t}{\omega^2} \tag{32}$$

Its shape is shown in Fig. 1

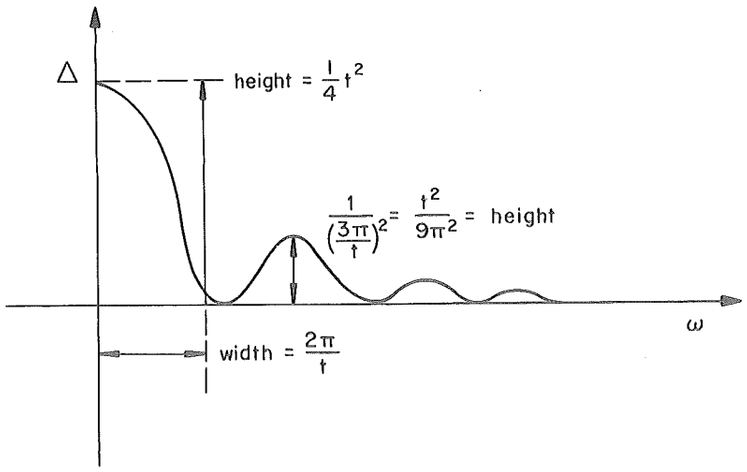


Figure 1

$$\text{area} \sim \frac{1}{4}t^2 \times \frac{2\pi}{t} \to \frac{\pi}{2}t$$

Actually,

$$\lim_{t\to\infty} \Delta(\omega, t) = \frac{\pi}{2}\, t\, \delta(\omega) \tag{33}$$

So the transition probability from n to m in t is

$$4\lambda^2 |V_{mn}|^2 \Delta(\omega, t) + 0(\lambda^3) \tag{34}$$

and as t gets very long this approaches

$$\to 4\lambda^2 |V_{mn}|^2 \frac{\pi}{2}\, t\, \delta(\omega_{mn}) \tag{35}$$

So, for large t we get for the transition probability during t,

$$t W_{mn} \tag{36}$$

with our earlier "Golden Rule" definition of W_{mn}.

But now we have to understand how to interpret the limit.

(1) t is never actually infinite, so the delta function is never exact. However, the area is always exactly proportioned to t.

(2) The true energy eigenvalues are of the order of magnitude.

$$E_{\text{time, m}} = E_{\text{unperturbed, m}} + 0(\lambda^2)$$

(This comes from perturbation theory). "Because true total energy is conserved" we expect that

$$E_m + 0(\lambda^2) = E_n + 0(\lambda^2)$$

or

$$\omega_{mn} = 0(\lambda^2) \tag{37}$$

for the physically possible transitions. This means that, for small λ,

$$\omega_{mn} t = 0(\lambda^2 t) \tag{38}$$

But for ω to be inside the first peak of the function $\Delta(\omega, t)$, we require

$$|\omega t| \lesssim 0(2\pi)$$

or, for typical values of ω,

$$0(\lambda^2 t) \lesssim 0(2\pi) = 0(1) \tag{39}$$

So, by picking $\lambda^2 t$ small enough, even with λ small and t large, we are usually within the main peak of $\Delta(\omega, t)$.

(3) A third point in the standard derivation is to suppose that the unperturbed spectrum is quite dense. For example, in a many body system with N particles, the number of states within any internal $d\omega$ is of the order

$$N\rho(\omega)\, d\omega \tag{40}$$

where $\rho(\omega)$ is a density of states, of order (1) as $N \to \infty$. So, for large N, there will be many unperturbed states within the range

$$\omega_{mn} = 0(\lambda^2) \tag{41}$$

These all have roughly the same unperturbed energy. Let's now sum over these (final) states

$$\sum_{\omega_{mn}=0(\lambda^2)}{}' |(e^{-it\hat{H}})_{mn}|^2$$

$$= \sum_{\omega_{mn}=0(\lambda^2)} 4\lambda^2 |V_{mn}|^2 \Delta(\omega_{mn}, t) \tag{42}$$

$$\to \int d\omega_{mn}\, N\rho(\omega_m)\, 4\lambda^2 |V_{nm}|^2 \Delta(\omega_{mn}, t)$$

Now, suppose that $\rho(\omega)$ and V_{nm} are "smooth" functions of ω_{mn} over the range

$$\omega_{mn} = 0(\lambda^2)$$

Then, for large t we can replace the integral by

$$N\rho(\omega_m)\, 4\lambda^2 |V_{nm}|^2 \int d\omega_{mn}\, \Delta(\omega_{mn}, t) \tag{43}$$

But the latter integral is known, exactly, so we get

$$\to \underbrace{N\rho(\omega_m)\, 2\pi\lambda^2 |V_{nm}|^2}_{W_{mn}} \times t \tag{44}$$

And we have here just another form of W_{mn}

In deriving the expression we used the following order of magnitude estimates

(1) λ small
(2) t large
(3) $\lambda^2 t < 0(2\pi)$
(4) $\omega_{mn} = 0(\lambda^2)$
(5) $\rho(\omega) = 0(1)$ as $N \to \infty$

Note especially the third estimate. This will come up again in Van Hove's derivation.

Having found a transition probability proportioned to t, we get a time independent transition rate,

$$\text{rate} = \frac{d}{dt}(\text{prob.}) \tag{45}$$

This concludes our survey of the old-fashioned derivations of Pauli's master equations.

LECTURE I

Part 2

VAN HOVE'S CONTRIBUTIONS

Van Hove made two principal contributions to the modern theory of the master equation. His first (1955) was a more careful and rigorous derivation of Pauli's equation, for small λ only. His later contribution (1957) and (1959) was a generalization to higher orders in λ. Let's consider the first now.

We need the full perturbation expansion of (26), obtained by iterating (27),

$$e^{-it\hat{H}} = e^{-it\hat{H}_0} - i\int_0^t dt_1\, e^{-i(t-t_1)\hat{H}_0}\, \lambda\hat{V}\, e^{-it_1\hat{H}_0}$$

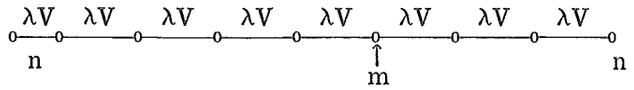
$$+ (-i)^2 \int_0^t dt_1 \int_0^t dt_2\, e^{-i(t-t_1)\hat{H}_0}\, \lambda\hat{V}\, e^{-i(t_1-t_2)\hat{H}_0}\, \lambda\hat{V}\, e^{-it_2\hat{H}_0} \tag{46}$$

$$+ 0(\lambda^3)$$

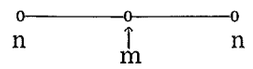
And, we need the square of the expansion, or

$$|(e^{-it\hat{H}})_{mn}|^2 = (e^{it\hat{H}})_{nm}(e^{-it\hat{H}})_{mn} \qquad (47)$$

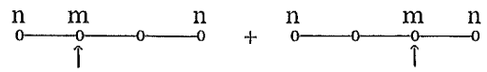
Any term in the expansion of the product can be indicated by a graph of the following sort,



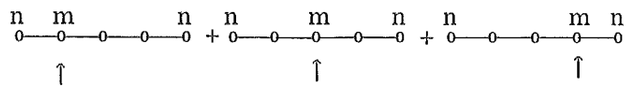
This particular one shows 5th order from the left and 3rd order from the right. The graph needed in the original Pauli theory is just



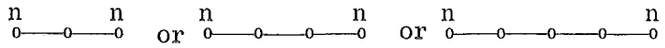
To the next order we get (for $n \neq m$)



and in the fourth order,



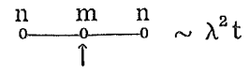
Now Van Hove observed that, for reasonable interactions of of the sort that we have had in mind all along, whenever one has a combination like



where all the interior indices are different from each other and different from n, then the integral gives asymptotically a factor t.

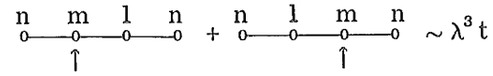
The reason for this is just the same as we saw in the earlier discussion: one gets a function of time that looks asymptotically like $t\,\delta(\omega)$, where the δ function is not really infinitely sharp, but only nearly so.

Note that the second order term has the character:



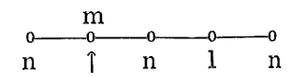
$\sim \lambda^2 t$

In third order we can have only



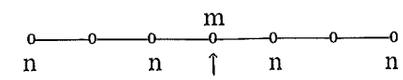
$\sim \lambda^3 t$

In fourth order, however, we get the possibility of



$\sim (\lambda^2 t)^2$

In sixth order we can get



$\sim (\lambda^2 t)^3$

And so on.
The important point here is that higher powers of t will occur, in fact the whole series looks asymptotically like

$$\begin{aligned} |\ |^2 = {} & (\ )\lambda^2 t + (\ )\lambda^3 t + (\ )^4\lambda\ t + \ldots \\ & + (\ )(\lambda^2 t)^2 + (\ )(\lambda^3 t)^2 + \ldots \\ & + (\ )(\lambda^3 t)^3 + (\ )(\lambda^3 t)^3 + \ldots \end{aligned} \qquad (48)$$

Van Hove noticed that the limit

$$\left.\begin{array}{l} \lambda \to 0 \\ t \to \infty \end{array}\right\} \quad \lambda^2 t = \text{constant} \qquad (49)$$

eliminated all but the set of powers of $\lambda^2 t$. In the limit, which is just like the one we used earlier,

$$|\ |^2 \to (\ )\lambda^2 t + (\ )(\lambda^2 t)^2 + (\ )(\lambda^2 t)^3 \ldots \qquad (50)$$

He then observed that upon differentiation,

$$\frac{d}{dt}|(e^{-itH})_{mn}|^2 = \sum_1{}' W_{n1}|(e^{-it\hat{H}})_{1m}|^2 - \sum_1{}' W_{1n}|(e^{-it\hat{H}})_{nm}|^2 \tag{51}$$

so that if we start out in the particular state m, and

$$\rho_{mn}(t) = |(e^{-it\hat{H}})_{nm}|^2 \tag{52}$$

we get

$$\frac{d\rho_{nn}}{dt} = \sum_1 (W_{n1}\rho_{11} - W_{11}\rho_{nn}) \tag{53}$$

But because of superpostion of initial conditions, the result, not containing m, is in fact independent of the choice of initial state.

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LECTURE II

Part 1

The second lecture will be devoted to Liouville operator techniques in quantum statistical mechanics.

First, we make a table of the standard notations. The "Liouville equation" is

$$\left\{ \begin{array}{l} \frac{\partial\hat{\rho}(t)}{\partial t} = -i[\hat{H}, \hat{\rho}(t)] \\ \\ \frac{\partial\rho_{mn}(t)}{\partial t} = -i\sum_1 (H_{m1}\rho_{1n}(t) - \rho_{m1}(t)\ H_{1n}) \end{array} \right\}$$

The formal solution is

$$\left\{ \begin{array}{l} \hat{\rho}(t) = e^{-it\hat{H}}\ \hat{\rho}(0)\ e^{+it\hat{H}} \\ \\ \rho_{mn}(t) = \sum_j \sum_k (e^{-it\hat{H}})_{mj}\rho_{jk}(0)\,(e^{+it\hat{H}})_{kn} \end{array} \right.$$

Resolvents and Laplace transforms: sometimes one wants to work with the Laplace transform of the density matrix.

Define

$$\hat{g}(s) = \int_0^\infty dt\ e^{-st}\hat{\rho}(t)$$

The transform of the equation of motion of $\hat{\rho}$ is

$$s\,\hat{g}(s) - \hat{\rho}(0) = -i[\hat{H},\ \hat{g}(s)]$$

$$sg_{mn}(s) - \rho_{mn}(0) = -i\sum_{1}[H_{m1}g_{1n}(s) - g_{m1}(s)H_{1n}]$$

The latter are linear equations for $g_{m1}(s)$ which can in principle be solved for g. The Laplace transform can be written by means of resolvents also. Let

$$\hat{R}(z) = \frac{1}{\hat{H} - z\hat{1}}$$

$$R_{mn}(z) = [(\hat{H} - z\hat{1})^{-1}]_{mn}$$

Note that the singularities of R come at the (real) eigenvalues of $\hat{H}$. So,

$$e^{\mp it\hat{H}} = \frac{1}{2\pi i}\oint dz\,\frac{e^{\mp itz}}{z - \hat{H}}$$

$$= -\frac{1}{2\pi i}\oint dz\, e^{\mp itz}\hat{R}(z)$$

where the contour encloses the part of the real axis occupied by the exact eigenvalues of $\hat{H}$.
Then

$$\hat{g}(s) = \int_0^\infty dt\, e^{-st}\, e^{-it\hat{H}}\hat{\rho}(0)\cdot\frac{-1}{2\pi i}\oint dz\, e^{itz}\,\hat{R}(z)$$

$$= \frac{-1}{2\pi i}\oint dz\int_0^\infty dt\, e^{-st}\, e^{izt}\, e^{-i\hat{H}t}\hat{\rho}(0)\,\hat{R}(z)$$

$$= \frac{-1}{2\pi i}\oint dz\ \frac{1}{s - iz + i\hat{H}}\ \hat{\rho}(0)\,\hat{R}(z)$$

$$= -\frac{1}{2\pi i}\oint dz\cdot -i\,\hat{R}(z - is)\hat{\rho}(0)\,\hat{R}(z)$$

where the integration has to be taken around the poles of

$\hat{R}(z)$ only. So

$$\hat{g}(s) = \frac{1}{2\pi}\oint dz\,\hat{R}(z - is)\,\hat{\rho}(0)\ \hat{R}(z)$$

gives the Laplace transform of the density matrix in terms of Resolvents.

This equation is equivalent to the starting point of Van Hove's general derivation of the master equation. The only difference is that he uses Fourier transforms instead of Laplace transforms.

The inversion of a Laplace transform is

$$\hat{\rho}(t) = \frac{1}{2\pi i}\int_{\epsilon - i\infty}^{\epsilon + i\infty} ds\, e^{st}\,\hat{g}(s)$$

with a contour to the right of all singularities of $\hat{g}(s)$.

Van Hove does a perturbation expansion on the two resolvents and then collects terms and inverts the transform.

Now we want to rewrite all these formulas in the "Liouville Operator" notation.

$$\frac{\partial\hat{\rho}}{\partial t} = -i\,[\hat{H},\ \hat{\rho}(t)] = -i\,L\,\hat{\rho}(t)$$

where (for arbitrary operator $\hat{A}$)

$$\hat{B} = L\hat{A} = [\hat{H},\ \hat{A}]$$

This is a linear operator that turns an operator $\hat{A}$ into a new operator $\hat{B}$.

With subscripts,

$$\frac{\partial\rho_{mn}}{\partial t} = -i\sum_{m'}\sum_{n'} L_{mn\,m'n'}\,\rho_{m'n'}$$

$$L_{mn\,m'n'} = H_{mm'}\delta_{nn'} - H_{n'n}\,\delta_{mm'}$$

$$= H_{mm'}\,\delta_{nn'} - \delta_{mm'}\,(H^*)_{nn'}$$

The operator L can be regarded as a <u>tetradic</u> operator (four subscripts). The multiplication rule for tetradics is

$$(L_1 L_2)_{mnm'n'} = \sum_k \sum_l (L_1)_{mnkl} (L_2)_{klm'n'}$$

The identity tetradic is

$$(1)_{mnm'n'} = \delta_{mm'} \delta_{nn'}$$

so that

$$(1 \cdot \hat{A})_{mn} = \sum_{m'} \sum_{n'} (1)_{mnm'n'} A_{m'n'} = A_{mn}$$

and

$$(1 \cdot L)_{mnm'n'} = L_{mnm'n}$$

Evidently tetradics behave much like matrices. In fact, one can reduce their algebra to that of ordinary matrices by the following trick.

We start by representing operators by matrices

$$\hat{A} \rightarrow A_{mn}$$

Next, we pick some ordering sequence for the subscripts, for example

$$\alpha = 1 \longleftrightarrow (m, n) = (11)$$
$$\alpha = 2 \longleftrightarrow (m, n) = (12)$$
$$\alpha = 3 \longleftrightarrow (m, n) = (21)$$
$$\alpha = 4 \longleftrightarrow (m, n) = (13)$$
$$\alpha = 5 \longleftrightarrow (m, n) = (22)$$
$$\alpha = 6 \longleftrightarrow (m, n) = (31)$$
$$\alpha = 7 \longleftrightarrow (m, n) = (14)$$
$$\alpha = 8 \longleftrightarrow (m, n) = (23)$$
$$\alpha = 9 \longleftrightarrow (m, n) = (32)$$
$$\alpha = 10 \longleftrightarrow (m, n) = (41)$$

etc.

So we identify

$$\hat{A} \rightleftarrows A_{mn} \rightarrow A_{(\alpha)} \rightarrow \text{"vector } \vec{A}\text{"}$$

Then the formula

$$\hat{B} = L\hat{A}$$

can be written as

$$B_{(\alpha)} = \sum_{\beta=1}^{\infty} L_{(\alpha)(\beta)} A_{(\beta)} \qquad (\alpha = 1, 2, 3, \ldots)$$

so that $L_{(\alpha)(\beta)}$ behaves like a matrix of two subscripts.

This means that (with due caution!) the algebra of L can be reduced to the algebra of matrices.

Now let's return to Liouville equation,

$$\frac{\partial \hat{\rho}}{\partial t} = iL\hat{\rho}(t)$$

This has the solution

$$\hat{\rho}(t) = e^{-itL} \hat{\rho}(0)$$

where

e^{-itL} is a tetradic operator,

$$e^{-itL} = \sum_0^{\infty} \frac{(-it)^n}{n!} L^n$$

Because we have defined the multiplication of L, this is a good quantity. The component form is

$$\rho_{mn}(t) = \sum_{m'} \sum_{n'} (e^{-itL})_{mnm'n'} \rho_{m'n'}(0)$$

These are to be compared with the traditional forms

$$\hat{\rho}(t) = e^{-it\hat{H}} \hat{\rho}(0) \; e^{+it\hat{H}}$$

$$\rho_{mn}(t) = \sum_{m'} \sum_{n'} (e^{-it\hat{H}})_{mm'} \rho_{m'n'}(0) (e^{it\hat{H}})_{nn'}$$

so we see that

$$(e^{-itL})_{mnm'n'} = (e^{-it\hat{H}})_{mm'} (e^{it\hat{H}})_{nn'}$$

Let's verify the first power of t just for fun.

$$(\text{LHS}) = (1)_{mnm'n'} - itL_{mnm'n'} + \dots$$
$$= \delta_{mm'}\delta_{nn'} - itH_{mm'}\delta_{nn'}$$
$$+ it\,\delta_{mm'}H_{n'n} + 0(t^2)$$

Now do

$$\text{RHS} = (\hat{1} - it\hat{H})_{mm'}(1 + itH)_{n'n}$$
$$= (\delta_{mm'} - itH_{mm'} + \dots)(\delta_{nn'} + itH_{n'n} + \dots)$$
$$= \delta_{mm'}\delta_{nn'} - itH_{mm'}\delta_{nn'} + it\,\delta_{mm'}H_{n'n} + \dots$$

So RHS = LHS to order t. Obviously this must be true to all orders.

To go further, we can do perturbation expansions with L

if $\hat{H} = \hat{H}_0 + \hat{H}_1$ then clearly

$$L = L_0 + L_1$$

The operator e^{-itL} obeys the integral equation

$$e^{-itL} = e^{-itL_0} - i\int_0^t dt_1\, e^{-i(t-t_1)L_0}\, L_1 e^{-itL}$$

which gives, on differentiation,

$$\frac{d}{dt}e^{-itL} = -iLe^{-itL}$$

as it should. We can use the integral equation by iteration to get

$$e^{-itL} = e^{-itL_0} - i\int_0^t dt_1\, e^{-i(t-t_1)L_0}\, L_1 e^{-it_1L_0}$$
$$+ (-i)^2\int dt_1\int dt_2\, e^{-i(t-t_2)L_0}\, L_1 e^{-i(t_1-t_2)L_0}\, L_1 e^{-it_2L_0}$$

etc.

This is all just as one would do with Hamiltonian operators. It has the advantage, however, that the perturbation comes always in one place. Compare this with the expansion of

the standard form

$$e^{-itH}\hat{\rho}(0)\,e^{+it\hat{H}}$$

where one gets $\hat{H}_1$ on both sides of $\hat{\rho}(0)$.

But the real advantage appears in the resolvent form. From

$$\hat{g}(s) = \int_0^\infty dt\, e^{-st}\,\hat{\rho}(t)$$

we get

$$s\hat{g}(s) - \hat{\rho}(0) = -iL\,\hat{g}(s)$$

"Solve" this for $\hat{g}$,

$$\hat{g}(s) = \frac{1}{s + iL}\,\hat{\rho}(0)$$

This is very much neater than the earlier

$$\hat{g}(s) = \frac{1}{2\pi}\oint dz\,\hat{R}(z - is)\hat{\rho}(0)\,\hat{R}(z)$$

Note also that this connects with the formal solution:

$$g\quad \hat{g}(s) = \int_0^\infty dt\, e^{-st}e^{-itL}\hat{\rho}(0) = \frac{1}{s + iL}\,\hat{\rho}(0)$$

and we get this also by inverting the Laplace transform. Finally, observe the identity

$$\frac{1}{s + i(L_0+L_1)} = \frac{1}{s + iL_0} - i\,\frac{1}{s + iL_0}L_1\,\frac{1}{s + i(L_0+L_1)}$$

which iterates to the perturbation expansion

$$= \frac{1}{s + iL_0} - i\,\frac{1}{s + iL_0}L_1\,\frac{1}{s + iL_0}$$
$$+ (i)^2\,\frac{1}{s + iL_0}L_1\,\frac{1}{s + iL_0}L_1\,\frac{1}{s + iL_0} - 0(L_1^3)$$

So much for the generalities of notation.

LECTURE II

Part 2

Next, we consider the derivation of the master equation. What we want is the diagonal part of the density matrix. Let's introduce a projection operator D to select the diagonial part.

$$(D\hat{\rho})_{mn} \equiv \rho_{mm}\,\delta_{mn}$$

This operation can be represented explicitly by a tetradic,

$$D_{mnm'n'} = \delta_{mm'}\,\delta_{nn'}\,\delta_{mn}$$

which evidently has the desired character. Similarly, the operator that selects the non-diagonal part is 1 - D, where

$$(1 - D)_{mnm'n'} = \delta_{mm'}\,\delta_{nn'}\,(1 - \delta_{mn}),$$

Now we use D and 1 - D to separate the Liouville equation into two parts,

$$D\,s\,\hat{g}(s) - D\hat{\rho}(0) = -iDL\hat{g}(s)$$

$$(1 - D)\,s\hat{g}(s) - (1 - D)\hat{\rho}(0) = -i(1 - D)\,L\hat{g}(s)$$

For convenience in notation we write

$$\hat{g}(s) = \hat{g}_1(s) + \hat{g}_2(s)$$
$$\hat{g}_1(s) = D\hat{g}(s)$$
$$\hat{g}_2(s) = (1 - D)\,\hat{g}(s)$$

Then the two parts of Liouville equation contain $\hat{g}_1$ and $\hat{g}_2$,

$$s\hat{g}_1(s) - \hat{\rho}_1(0) = -iDL\hat{g}_1(s) - iDL\hat{g}_2(s)$$
$$s\hat{g}_2(s) - \hat{\rho}_2(0) = -i(1 - D)\,\hat{g}_1(s)\,L - i(1 - D)\,L\hat{g}_2(s)$$

Solve the second equation for $\hat{g}_2$:

$$[s + i(1 - D)\,L]\hat{g}_2 = \hat{\rho}_2(0) - i(1 - D)\,L\hat{g}_1$$

$$\hat{g}_2 = \frac{1}{s + i(1 - D)\,L}\,\hat{\rho}_2(0) - \frac{1}{s + i\,(1 - D)\,L}\,(1 - D)\;L\hat{g}_1$$

Put this back in the first equation,

$$s\hat{g}_1(s) + iDL\hat{g}_1(s) = \hat{\rho}_1(0)$$

$$- iDL\,\frac{1}{s + i(1 - D)\,L}\,\hat{\rho}_2(0)$$

$$- DL\,\frac{1}{s + i(1 - D)\,L}\,(1 - D)\,L\hat{g}_1(s)$$

Note that the equation relates $\hat{g}_1(s)$ to itself and to <u>both initial parts.</u>

Next we invert the Laplace transform. The only tricky point here is that the inverse transform of a product is a convolution,

$$\int_0^\infty dt e^{-st} \int_0^t dt_1\; a(t_1)\,b(t - t_1)$$

$$= \int_0^\infty dt e^{-st}\,a(t) \cdot \int_0^\infty dt'\; e^{-st'} b(t')$$

So the equation for $\hat{g}_1$ gives

$$\frac{d\hat{\rho}_1(t)}{dt} = - iDL\hat{\rho}_1(t) - iDLe^{-i(1-D)Lt}\;\;\hat{\rho}_2(0)$$

$$-\int_0^t dt_1 \left[DLe^{-it_1(1-D)L}\;\;(1 - D)\,L \right] \hat{\rho}_1(t - t_1)$$

The exciting thing here is that when the non-diagonal part vanishes initially,

$$\hat{\rho}_2(0) = 0$$

or the density matrix is initially diagonal, then we have an equation that contains $\hat{\rho}_1$ only. Even though the non-diagonal part will generally not vanish after t = 0 we don't have to know what it is.
The quantity

$$g(t) = e^{-i(1-D)Lt}$$

can be interpreted two ways:

(1) As the solution of

$$\frac{dg}{dt} = -i(1 - D)Lg$$

and (2) by the expansion

$$g = 1 - i(1 - D)LD + \frac{i^2}{2}(1 - D)L(1 - D)Lt^2 \ldots$$

The general master equation is therefore

$$\frac{d\hat{\rho}_1(t)}{dt} = - iDL\hat{\rho}_1(t) - \int_0^t dt_1 K(t_1)\hat{\rho}_1(t - t_1)$$

when $\hat{\rho}_2(0) = 0$ and

$$K(t_1) = DLe^{-i(1-D)Lt_1}(1 - D)L$$

Now we take components

$$<n|\hat{\rho}_1(t)|n> = \rho_{nn}(t)$$

and

$$\frac{d\rho_{nn}(t)}{dt} = - i[L\hat{\rho}(t)]_{nn} - \int_0^t dt_1 [K(t_1)\hat{\rho}_1(t - t_1)]_{nn}$$

The first part of the RHS vanishes. This is how:

$$[L\hat{\rho}_1]_{nn} = \sum_a \sum_b L_{nnab}(\hat{\rho}_1)_{ab} = \sum_a L_{nnaa}\rho_{aa}$$

But

$$L_{mnaa} = H_{na}\delta_{na} - \delta_{na}H_{an}$$
$$= (H_{aa} - H_{aa})\delta_{na} = 0$$

This gives:

$$\frac{d\rho_{nn}(t)}{dt} = - \int_0^t dt_1 [K(t_1)\cdot\hat{\rho}_1(t - t_1)]_{nn}.$$

To finish this we write

$$[K\cdot\hat{\rho}_1]_{nn} = \sum_c \sum_d K_{nncd}(\hat{\rho}_1)_{cd}$$
$$= \sum_m K_{nnmm}\rho_{mm}$$

Thus,

$$\frac{d\rho_{nn}(t)}{dt} = - \sum_m \int_0^t dt_1 K_{nnmm}\rho_{mm}$$

This is beginning to look like a master equation.
Lets work out K in detail, step by step

$$K_{nnmm}(t) = [Le^{-it_1(1-D)L}(1 - D)L]_{nnmm}$$

First, note that

$$[LX]_{nnmm} = \Sigma\Sigma L_{nncd}X_{cdnm}$$
$$= \Sigma\Sigma L^0_{nncd}X_{cdmm} + \Sigma\Sigma L^1_{nncd}X_{cdmm}$$

look at the L^0 part,

$$\Sigma\Sigma(H^0_{nc}\delta_{nd} - \delta_{nc}H^0_{dn})X_{cdmm}$$
$$= \Sigma\Sigma(E_n\delta_{nc}\delta_{nd} - E_n\delta_{nc}\delta_{nd})X_{cdmm} = 0$$

So only L_1 appears, and

$$K_{nnmm} = [L_1 e^{-it_1(1-D)L}(1 - D)L]_{nnmm}$$

Coming in from the other end, we find

$$[(1 - D)L]_{abmm} = (1 - \delta_{ab})L_{abmm}$$

$$= (1 - \delta_{ab})(L^0_{abmm} + L^1_{abmm})$$

The L_0 part vanishes,

$$L^0_{abmm} = E_a \delta_{am}\delta_{bm} - E_m \delta_{mb}\delta_{am} = 0$$

This gives

$$K_{nnmm} = [L_1 e^{-it_1(1-D)L} \quad (1 - D)L_1]_{nnmm}$$

Note that it is formally of order λ^2

Next we prove the sum rule

$$\sum_m K_{nnmm} \equiv 0 \qquad \text{all n, all t}$$

This is because of

$$\sum_m K_{nnmm} = \sum_m \sum_c \sum_d [L_1 e^{-it_1(1-D)L} \quad (1 - D)]_{nncd} \cdot L_{cdmm}$$

$$= \sum_c \sum_d [L_1 e^{-it_1(1-D)L} \quad (1 - D)]_{nncd} \cdot \sum_m L_{cdmm}$$

But

$$\sum_m L_{cdmm} = \sum_m H_{cm}\delta_{dm} \cdot \sum_m \delta_{cm} H_{md} = H_{cd} - H_{cd} = 0$$

The sum rule can be used this way:

$$K_{nn,\,mm} = -\sum_{m \neq n} K_{nnmm}$$

and

$$\frac{d\rho_{nn}(t)}{dt} = -\sum_{m \neq n} \int_0^t dt_1 K_{nn,\,mm}(t_1)\,[\rho_{mm}(t_1) - \rho_{nn}(t_1)]$$

This begins to get very close to a master equation. If we had symmetry of K, we could get even closer.

The symmetry

$$K_{nn,\,mm}(t) = K_{mm,\,nn}(t)$$

follows easily from the structure of K, as is often observed in such problems, in the absence of magnetic field. The argument is as follows:

Note first that

$$L_{abcd} = H_{ac}\delta_{bd} - \delta_{ac}H_{db},$$

$$L_{cdab} = H_{ca}\delta_{bd} - \delta_{ac}H_{bd},$$

so that

$$L_{cd,\,ab} = L^*_{ab,\,cd}$$

But in the absence of magnetic fields (and spin effects) we can always choose real unperturbed eigenfunctions. Therefore it is always possible to have a representation in which H_{mn} is real, and

$$L_{cdab} = L_{abcd}$$

Next, we note that the unit tetradic and the operator D are symmetric in the same way, e.g.,

$$D_{abcd} = D_{cdab}$$

But

$$K = DL_1 \; e^{-it_1(1-D)L} \quad (1 - D)L_1$$

and each operator appearing with K is symmetric to the exchange of the left and right pairs of subscripts. This K has the same symmetry,

$$K_{nnmm} = K_{mmnn}$$

(This result should also follow from more elegant time-reversal arguments. We do not pursue this here.)
Now our almost-master equation can be written in the form

$$\frac{d\rho_{nn}(t)}{dt} = -\int_0^t dt_1 \sum_m \left[K_{nn,\,mm}(t_1)\rho_{mm}(t - t_1) - K_{mm,\,nn}(t_1)\rho_{nn}(t - t_1) \right]$$

The only extra feature we have here is the convolution over time. This appears also in Van Hove's generalized master equation, as well as in those of Resibois and Montroll.

Note that we do not have to bring in the symmetry of K; there is no reason why we cannot keep it always as K_{nnmm}.

LECTURE III

The generalized master equation that was just derived reduces, in the limit of weak interaction, to the Pauli master equation. This can be seen in the following way.

The essential quantity is

$$K_{nnmm}(t) = \left[L_1 e^{-it(1-D)L} \quad (1 - D) L_1 \right]_{nnmm}$$

Note that L_1 is of order λ. Let us take advantage of this explicitly by exposing all factors λ, or

$$L = L_0 + \lambda L_1$$

Then

$$K_{nnmm}(t) = \lambda^2 \left[L_1 e^{-it(1-D)(L_0+\lambda L_1)} \quad (1 - D) L_1 \right]_{nnmm}$$

Now we introduce a new time scale,

$$\lambda^2 t = \tau$$

$$\rho_{nn}(t) = P(\tau)$$

Consequently,

$$\frac{\partial P_n(\tau)}{\partial \tau} = -\sum_m \int_0^{\tau/\lambda^2} dt_1 \left[L_1 e^{-it_1(1-D)(L_0+\lambda L_1)} \quad (1 - D) L_1 \right]_{nnmm} \times \left\{ P_m(\tau - \lambda^2 t_1) - P_n(\tau - \lambda^2 t_1) \right\}$$

(We have not bothered here to invoke the symmetry of K.)

Now we just boldly take the limit $\lambda \to \infty$, for τ fixed. This gives

$$\frac{\partial P_n(\tau)}{\partial \tau} = \sum_m \int_0^\infty dt_1 \left[L_1 e^{-it_1(1-D)L_0} \quad (1 - D) L_1 \right]_{nnmm}$$

$$x \{P_m(\tau) - P_n(\tau)\}$$

This limit is the same one used by Van Hove:

$$\left.\begin{array}{l} \lambda \to 0 \\ t \to \infty \end{array}\right\} \qquad \lambda^2 t = \tau = \text{constant}$$

In the limit, we can return to the original notation,

$$\frac{\partial \rho_{nn}(t)}{\partial t} = + \sum_m W_{nm} [\rho_{mm}(t) - \rho_{nn}(t)]$$

where

$$W_{nm} = - \lambda^2 \int_0^\infty dt \left[L_1 e^{-it(1-D)L_0} \quad (1 - D) L_1 \right]_{nnmm}$$

Because of the limit, the integrand here contains

$$\exp - it(1 - D) L_0$$

where L_0 is the unperturbed operator. This is a great convenience in continuing the calculation.

The simplification here is that D Lo vanishes:

$$(DL_0)_{abcd} = \delta_{ab} [H^0_{ac} \delta_{bd} - \delta_{ac} H^0_{db}]$$

$$= \delta_{ab} [E_a \delta_{ac} \delta_{bd} - E_b \delta_{bd} \delta_{ac}]$$

Therefore,

$$(1 - D) L_0 = L_0$$

and

$$e^{-it(1-D)L_0} = e^{-itL_0}$$

But this gives the unperturbed time displacement operator, and we know how to handle it.

Recall from an earlier lecture that

$$(e^{-itL})_{mnm'n'} = (e^{-itH})_{mm'} (e^{itH})_{nn'}$$

For L = Lo, we get

$$(e^{-itL_0})_{mnm'n'} = e^{-itE_m} \delta_{mm'} e^{itE_n} \delta_{nn'}$$

$$= e^{-it(E_m - E_n)} \delta_{mm'} \delta_{nn'}$$

With this result we can work out all the operators in W_{nm}:

$$W_{mn} = - \lambda^2 \int_0^\infty dt \sum_{abcd} (L_1)_{nnab} (e^{-it(E_m - E_n)} \delta_{ac} \delta_{bd})$$

$$(L_1)_{cdmm}$$

Or,

$$W_{nm} = - \lambda^2 \int_0^\infty dt \sum_{ab} (V_{na} \delta_{nb} - \delta_{na} V_{bn}) e^{-it(E_a - E_b)}$$

$$x (V_{am} \delta_{bm} - \delta_{am} V_{mb})$$

$$= - \lambda^2 \int_0^\infty dt \sum_{ab} \{ V_{na} V_{am} \delta_{nb} \delta_{bm} e^{-it(E_a - E_b)}$$

$$+ V_{bn} V_{mb} \delta_{na} \delta_{ma} e^{-it(E_a - E_a)}$$

$$- V_{na} V_{mb} \delta_{nb} \delta_{am} e^{-it(E_a - E_a)}$$

$$- V_{bn} V_{am} \delta_{na} \delta_{bm} e^{-it(E_a - E_a)} \}$$

$$= -\lambda^2 \int_0^\infty dt \left\{ \sum_a V_{na} V_{an} \delta_{nm} e^{-it(E_a - E_m)} + \sum_b V_{bn} V_{nb} \delta_{nm} e^{-it(E_m - E_b)} - V_{nm} V_{mn} e^{-it(E_m - E_n)} - V_{mn} V_{nm} e^{-it(E_n - E_m)} \right\}$$

Because we need in general only $n \neq m$, the first two terms drop out. The second two terms combine to give

$$V_{nm} = +\lambda^2 |V_{nm}|^2 \int_0^\infty dt \left[e^{-it(E_m - E_n)} + e^{-it(E_n - E_m)} \right]$$

$$= 2\pi\lambda^2 |V_{nm}|^2 \delta(E_m - E_n) \Big]$$

Which is precisely the Golden Rule formula.

Notice that a swindle has been perpetrated. Namely, we come out with a delta function in energy, without also introducing the concept of a continuous spectrum. For a finite system (finite volume, finite number of particles) the spectrum is discrete and the delta function as it appears here is meaningless.

There are two ways out. One is to take the limit of infinite system before taking the Van Hove limit

$$\lambda \to 0, \quad t \to \infty, \quad \lambda^2 t = \text{constant}$$

This appears to provide the necessary continuous spectrum.

The other way out, which is actually more informative, is to keep the finite system and to also keep t finite. Now we have to return to the non-Markoffian equation, but as we have already found K to the second order, we put it in.

$$\frac{d\rho_{nn}(t)}{dt} = \lambda^2 \int_0^t dt_1 \sum_m |V_{nm}|^2 \, 2 \cos(\omega_{mn} t_1)$$

$$\times \{ \rho_{mm}(t - t_1) - \rho_{nn}(t - t_1) \} + 0(\lambda^3)$$

Recall that the quantum number n really refers to the set of all quantum numbers needed to characterize the unperturbed state of a many-body system. The set n includes the unperturbed energy and also various occupation numbers, etc. Let's suppose that V_{nm} is a "smooth" function of these quantum numbers. Because

$$\frac{\partial \rho_{nn}}{\partial t}$$

is proportional to the "smooth" $|V_{nm}|^2$, we may also regard ρ_{nm} "smooth."

But there is one term in the master equation that is not smooth,

$$\cos(\omega_{mn} t_1)$$

If E_n is fixed, and we vary E_m, this will oscillate wildly if t_1 is large. Because of the oscillations, the sum over m will have a rather small value for large t_1. On the other hand, the sum will be large for small t_1.

What is large and small in this context?

Suppose that a typical value of ω_{mn}, for states for which $V_{nm} \neq 0$, is about $\bar{\omega}$.
Then large t_1 means

$$t_1 \gg \frac{1}{\bar{\omega}}$$

and small t_1 means

$$t_1 \ll \frac{1}{\bar{\omega}}$$

As an example, consider the scattering process in which two quasi-particles are annihilated and two others are created. Then $\hbar\bar{\omega}$ is of the order of a typical quasi-particle energy. For phonons in a crystal, $\bar{\omega}$ would be of the order of the Debye frequency. Anyhow, $\bar{\omega}$ is typically of an atomic order of magnitude, and not a macroscopic one. That means the important time scale for the "memory" t_1 is an atomic time scale.

But in a many-body system, $\rho(t)$ varies slowly with time; its own characteristic time scale is a macroscopic one—or at least one that is much longer than the previously mentioned atomic time scale. In fact, the time scale for $\rho(t)$ is inversely proportional to λ^2, and this has nothing to do with $\bar{\omega}$. Thus, for small λ, $\rho(t)$ will hardly change at all during the memory $1/\bar{\omega}$.

Because of this, we can safely approximate:

$$\rho_{nn}(t - t_1) \cong \rho_{nn}(t) \text{ for } t_1 \lesssim 0(1/\bar{\omega})$$

and

$$\frac{\partial \rho_{nn}(t)}{\partial t} \cong \lambda^2 \int_0^t dt_1 \sum_m |V_{nm}|^2 \cdot \cos \omega_{mn} t_1$$

$$x\{\rho_{mm}(t) - \rho_{nn}(t)\}$$

But now the t_1 integral can be done, giving

$$\frac{\partial \rho_{nn}(t)}{\partial t} \cong \lambda^2 \sum_m |V_{nm}|^2 \cdot 2 \frac{\sin \omega_{mn} t}{\omega_{mn}}$$

$$x\{\rho_{mm}(t) - \rho_{nn}(t)\}$$

For very large t the quality

$$\frac{\sin \omega_{mn} t}{\omega_{mn}}$$

looks very much like a delta function in ω; its actual width is of the order

$$\text{width} \sim 1/t.$$

We want to find many unperturbed states within this width, so that we can take limit of a large system with confidence.

In a many-body system the density of states is proportioned to the size of the system (either number of particles N or volume Ω.

The denisty of states is itself of order $1/\bar{\omega}$ because a typical ω_{nm} is of order $\bar{\omega}$. Therefore, the number of states in the interval 1/t is

$$\#\,\text{int} = 0 \left(N \cdot \frac{1}{\bar{\omega}} \cdot \frac{1}{t} \right)$$

and this should be much larger than 1 if we are to approximate $\frac{\sin \omega t}{\omega}$ by a delta function and still catch many states.

So, $\frac{N}{\bar{\omega} t} \gg 1$ or

$$t \ll N/\bar{\omega}$$

This limitation is not serious: by making N large, we can make the upper limit on t much larger than any time of experimental interest. The point is that, although t cannot actually become infinite as required in the Van Hove limit, nevertheless, the finite system, having N particles, behaves like the infinite system for a very long time. This is the justification for using the combination of delta function and continuous spectrum in the Pauli equation.

Finally, we note that the potential must have the property

$$\sum_m |V_{nm}|^2 \, x \, f_m = 0(N^0)$$

as $N \to \infty$. Here f_m is some arbitrary function of m. This requirement is a special case of what Van Hove calls the "diagonal singularity condition." Its consequence is that the transition rates W_{mn} are in fact independent of the size of the system—that is, the W_{mn} are intensive and not extensive properties. This expresses the macroscopic character of the processes described by the master equation.

In the derivation that I have just given, this diagonal singularity condition appears as a requirement that the results be physically sensible. In Van Hove's derivation, however, it is used to obtain the master equation in the first place.

Swenson has shown how Van Hove's derivation can be

carried out, like mine, without using the diagonal singularity condition until the very end, and then only for obtaining intensive transition rates.