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ON THE IDENTITY OF THREE GENERALIZED MASTER EQUATIONS

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Synopsis

Three apparently different quantum mechanical master equations, derived by Prigogine and Résibois, by Montroll, and independently by Nakajima and Zwanzig, are shown to be identical. The derivation by Zwanzig, based on projection operator and Liouville operator techniques, is repeated in greater detail than in previous articles. The results of Prigogine and Résibois, and of Montroll, are found by making changes in notation.

Introduction. Considerable attention has been given in recent years to the rigorous derivation of quantum mechanical master equations, valid to all orders in a perturbation. This article contains a demonstration of the identity of three apparently different results.

Four exact master equations have been found (to the best of my knowledge). In chronological order, they are as follows:

The first was obtained by Van Hove [1]) in 1957. Although his derivation was based on the limit of an infinite system, and in particular, on his diagonal singularity condition, the same equation has been obtained by Swenson [2]) without making any assumptions at all about the nature of the system. This equation is referred to as VHS in the following.

The second master equation was obtained by Nakajima [3]) in 1958, and independently and in greater detail by myself [4]) [5]) in 1960. Both derivations used projection operator and Liouville operator methods. The resulting master equation is referred to here as NZ.

The third master equation was derived by Résibois [6]) in 1961. His method of derivation was modified in a subsequent article by Prigogine and Résibois [7]), also in 1961. The final result is given explicitly in a 1963 article by Résibois [8]), where he refers to it as a master equation derived by Prigogine and Résibois; so we refer to it as PR.

The fourth master equation was derived by Montroll [9]) in 1961. An earlier article [10]) in 1960 gave the derivation to lowest order in the perturbation, and suggested the general approach.

In a recent article [8]) Résibois discussed the relation between VHS and

PR. He concluded that both equations were exact, and that they both could be used to calculate the same quantities, but that they were not identical. Résibois did not mention, however, the other master equations NZ and M.

The main purpose of the present article is to show that PR and M, while apparently different in structure from NZ, are actually identical with NZ aside from differences in notation. Specifically, M is obtained from NZ by using determinants and minors to calculate (formally) the inverse of a certain tetradic operator. Also, PR is obtained from NZ by replacing matrix subscripts (m, n) by their difference and their arithmetic mean. Thus, the results of this article, taken together with those of ref. 8, can be summarized in the equation NZ = PR = M $\neq$ VHS.

A secondary purpose of the present article is to call attention once more to the methods used to derive NZ, and to go into greater detail concerning the derivation than seemed desirable in my previous articles. These methods were devised in the first place to be fast and economical, so that one would not have to go through complicated and tedious arguments of the sort found in refs. 6 and 7. While concise and direct, these methods involve a certain amount of unfamiliar and abstract operator technique. It is hoped that the following detailed exposition will serve to make them more accessible and easily used.

Liouville operators and von Neumann's equation. The master equations with which we are concerned are kinetic equations for the diagonal elements of a density matrix. The density operator is $\hat{\rho}$; its matrix elements in some particular representation are ρ_{mn}.

The time dependence of the density matrix $\rho_{mn}(t)$ is determined by von Neumann's equation. In operator form, this is (with $\hbar = 1$)

$$\frac{\partial \hat{\rho}}{\partial t} = -i\,(\hat{H}\hat{\rho} - \hat{\rho}\hat{H}), \tag{1}$$

where $\hat{H}$ is the Hamiltonian operator. In the chosen representation, von Neumann's equation is

$$\frac{\partial \rho_{mn}}{\partial t} = -i \sum_l (H_{ml}\,\rho_{ln} - \rho_{ml}\,H_{ln}). \tag{2}$$

We wish to extract from this an equation, determining the time dependence of the diagonal elements of $\hat{\rho}$, which does not contain the nondiagonal elements of $\hat{\rho}$.

We solve von Neumann's equation by means of Liouville operators. These operators are defined as follows. Given an arbitrary operator $\hat{A}$, another operator $\hat{C}$ can be constructed by the rule

$$\hat{C} = (\hat{H}\hat{A} - \hat{A}\hat{H}). \tag{3}$$

In Heisenberg quantum mechanics this is tantamount to turning an operator into its time derivative. The operation of going from $\hat{A}$ to $\hat{C}$ will be denoted by L, and L will be called the Liouville operator,

$$\hat{C} = L\hat{A}. \tag{4}$$

It is clearly a linear operation. In the chosen representation it turns a matrix with two subscripts into another matrix with two subscripts; therefore, it can be represented by a *tetradic* with four subscripts,

$$C_{mn} = \sum_{m'} \sum_{n'} L_{mnm'n'} A_{m'n'}. \tag{5}$$

Because of the definition of L as the commutator with $\hat{H}$, the explicit form of the tetradic L is

$$L_{mnm'n'} = H_{mm'} \delta_{nn'} - \delta_{mm'} H_{n'n}. \tag{6}$$

The multiplication rule for tetradics

$$(L_1 L_2)_{mnm'n'} = \sum_{a} \sum_{b} (L_1)_{mnab} (L_2)_{abm'n'} \tag{7}$$

can be found by evaluating repeated commutators. The identity tetradic is evidently

$$(1)_{mnm'n'} = \delta_{mm'} \delta_{nn'}. \tag{8}$$

Tetradics behave very much like ordinary matrices. In fact, their algebra can be reduced to that of matrices by the following trick. In representing an operator by a matrix, we may pick some arbitrary way of ordering pairs of subscripts, so that the pair (m, n) is denoted by a single integral subscript (α). In this way the matrix A_{mn} is replaced by the linear array or vector $A_{(\alpha)}$. Equation (5) can now be written as

$$C_{(\alpha)} = \sum_{(\beta)} L_{(\alpha)(\beta)} A_{(\beta)}. \tag{9}$$

We see that the tetradic L has been replaced by a matrix with two subscripts.

This means that the algebra of tetradics is isomorphic to the algebra of matrices. For finite tetradics, e.g. for interacting spin systems, the isomorphism is perfect. For infinite tetradics, convergence difficulties can arise as a result of the completely arbitrary ordering of subscript pairs. On this account we assume, as is customary in theoretical physics, that all infinite series converge unless there is good reason to believe otherwise; and we do not go into this question further.

We show later that the representation used by Résibois [6]) has an especially attractive property: the tetradic L is diagonal in a pair of bsu-

scripts. Because of this circumstance, he is able to use more conventional methods involving matrices with two subscripts.

In the Liouville operator notation, von Neumann's equation is

$$\frac{\partial \hat{\rho}}{\partial t} = -iL\hat{\rho}. \tag{10}$$

It has the formal solution, as an initial value problem,

$$\hat{\rho}(t) = \mathrm{e}^{-itL}\,\hat{\rho}(0). \tag{11}$$

The tetradic operator $\exp(-itL)$ is just as well defined as the more familiar $\exp(-it\hat{H})$. It can be calculated by expansion of the exponential function, followed by use of tetradic multiplication to get the powers of L. The useful identity

$$(\mathrm{e}^{-itL})_{mnm'n'} = (\mathrm{e}^{-it\hat{H}})_{mm'}\,(\mathrm{e}^{it\hat{H}})_{nn'} \tag{12}$$

can be verified by differentiation with respect to time, and application of eq. (6). On applying this identity to eq. (11) we get the familiar Heisenberg solution

$$\hat{\rho}(t) = \mathrm{e}^{-it\hat{H}}\,\hat{\rho}(0)\,\mathrm{e}^{it\hat{H}}. \tag{13}$$

The Liouville operator solution has two advantages over the usual Heisenberg operator solution. One advantage is the extra compactness in performing perturbation expansions. We divide the Hamiltonian $\hat{H}$ into an unperturbed part $\hat{H}_0$ and a perturbation $\hat{H}_1$,

$$\hat{H} = \hat{H}_0 + \hat{H}_1. \tag{14}$$

The perturbation expansion of $\exp(-it\hat{H})$ is well known,

$$\begin{aligned}\mathrm{e}^{-it\hat{H}} = \mathrm{e}^{-it\hat{H}_0} &- i\int_0^t \mathrm{d}t_1\,\mathrm{e}^{-i(t-t_1)\hat{H}_0}\,\hat{H}_1\,\mathrm{e}^{-it_1\hat{H}_0} + \\ &+ (-i)^2\int_0^t \mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\,\mathrm{e}^{-i(t-t_1)\hat{H}_0}\,\hat{H}_1\,\mathrm{e}^{-i(t_1-t_2)\hat{H}_0}\,\hat{H}_1\,\mathrm{e}^{-it_2\hat{H}_0} \\ &+ \ldots\ldots\end{aligned} \tag{15}$$

When this is applied to eq. (13), the perturbation appears on both sides of $\hat{\rho}(0)$. To collect terms of the n-th order in the perturbation, one must combine contributions of various orders from the two sides.

But we may divide L into an unperturbed part L_0 and a perturbation L_1,

$$L = L_0 + L_1. \tag{16}$$

The perturbation expansion of $\exp(-itL)$ has exactly the same structure as

that of $\exp(-it\mathscr{H})$,

$$e^{-itL} = e^{-itL_0} - i\int_0^t dt_1\, e^{-i(t-t_1)L_0} L_1 e^{-it_1 L_0} + \\ + (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2\, e^{-i(t-t_1)L_0} L_1 e^{-i(t_1-t_2)L_0} L_1 e^{-it_2 L_0} + \quad (17) \\ + \ldots .$$

When this expansion is applied to eq. (13), the perturbation always appears on the left of $\hat{\rho}(0)$, and it is not necessary to collect and combine contributions from two sides.

But the real advantage of the Liouville operator solution lies in the *resolvent* form of solution. Let us solve von Neumann's equation by means of Laplace transforms. The transform of the density operator $\hat{\rho}$ is denoted by $\hat{g}(p)$,

$$\hat{g}(p) = \int_0^\infty dt\, e^{-pt} \hat{\rho}(t). \quad (18)$$

On transforming eq. (10), we get

$$p\hat{g}(p) - \hat{\rho}(0) = -iL\, \hat{g}(p). \quad (19)$$

The formal operator solution is

$$\hat{g}(p) = \frac{1}{p + iL} \hat{\rho}(0). \quad (20)$$

This is very much simpler than the Laplace transform solution using Hamiltonians. If we define the resolvent of the Hamiltonian by

$$R(z) = \frac{1}{\hat{H} - z}, \quad (21)$$

then the solution $\hat{g}(p)$ is given by

$$\hat{g}(p) = \frac{1}{2\pi} \oint dz\, R(z - ip)\, \hat{\rho}(0)\, R(z). \quad (22)$$

The contour of integration in the z plane encloses that part of the real axis occupied by the exact eigenvalues of $\hat{H}$.

Equation (22) is equivalent to the starting point of Van Hove's derivation; the only difference is the trivial one that we have taken the Laplace transform where he took the Fourier transform.

Separation into relevant and irrelevant parts. The derivation given in refs. (3), (4), and (5) was based on the separation of the density operator into relevant and irrelevant parts by means of a projection operator. The

relevant part is clearly the diagonal part of $\hat{\rho}$; and the irrelevant part is the nondiagonal part of $\hat{\rho}$.

To select the diagonal part, we use the projection operator D. In tetradic form, D is

$$\begin{aligned}(D\hat{\rho})_{mn} &= \rho_{mm}\,\delta_{mn},\\ D_{mnm'n'} &= \delta_{mn}\,\delta_{mm'}\,\delta_{nn'}.\end{aligned} \tag{23}$$

It is easy to verify that this has the desired property, and that it obeys the fundamental requirement of a projection, $D^2 = D$. The irrelevant or nondiagonal part is selected by the projection operator $1-D$.

Thus the density operator separates into the diagonal part $\hat{\rho}_1$ and the nondiagonal part $\hat{\rho}_2$,

$$\begin{aligned}\hat{\rho} &= \hat{\rho}_1 + \hat{\rho}_2,\\ \hat{\rho}_1 = D\hat{\rho}, &\qquad \hat{\rho}_2 = (1-D)\hat{\rho}.\end{aligned} \tag{24}$$

In just the same way, the Laplace transform $\hat{g}(p)$ separates into diagonal and nondiagonal parts,

$$\begin{aligned}\hat{g}(p) &= \hat{g}_1(p) + \hat{g}_2(p),\\ \hat{g}_1(p) = D\hat{g}(p), &\qquad \hat{g}_2(p) = (1-D)\,\hat{g}(p).\end{aligned} \tag{25}$$

Next, we use D and $1-D$ to separate von Neumann's equation into two parts,

$$\begin{aligned}Dp\hat{g}(p) - D\hat{\rho}(0) &= -iDL\,\hat{g}(p),\\ (1-D)\,p\hat{g}(p) - (1-D)\,\hat{\rho}(0) &= -i(1-D)\,L\hat{g}(p),\end{aligned} \tag{26}$$

or

$$\begin{aligned}p\hat{g}_1(p) - \hat{\rho}_1(0) &= -iDL\,\hat{g}_1(p) - iDL\hat{g}_2(p),\\ p\hat{g}_2(p) - \hat{\rho}_2(0) &= -i(1-D)L\hat{g}_1(p) - i(1-D)L\hat{g}_2(p).\end{aligned} \tag{27}$$

We solve the second equation for $\hat{g}_2(p)$,

$$\begin{aligned}[p + i(1-D)L]\,\hat{g}_2(p) &= \hat{\rho}_2(0) - i(1-D)L\,\hat{g}_1(p);\\ \hat{g}_2(p) = \frac{1}{p + i(1-D)L}\,\hat{\rho}_2(0) &- \frac{1}{p + i(1-D)L}\,i(1-D)L\,\hat{g}_1(p);\end{aligned} \tag{28}$$

and we put the solution back into the first equation,

$$\begin{aligned}p\hat{g}_1(p) - \hat{\rho}_1(0) = -iDL\,\hat{g}_1(p) - iDL\,&\frac{1}{p + i(1-D)L}\,\hat{\rho}_2(0) -\\ - DL\,&\frac{1}{p + i(1-D)L}\,(1-D)L\,\hat{g}_1(S).\end{aligned} \tag{29}$$

The result of the preceding derivation is the Laplace transforms of our

generalized master equation. Let us invert the transform, using the well known theorem that the inverse of a product is a convolution. The result is

$$\frac{d\hat{\rho}_1(t)}{dt} = -iDL\,\hat{\rho}_1(t) - iDL\,e^{-i(1-D)Lt}\,\hat{\rho}_2(0) - \\ -\int_0^t dt_1\, DL\, e^{-it_1(1-D)L}(1-D)L\,\hat{\rho}_1(t-t_1). \tag{30}$$

In most applications of the master equation, the density operator is diagonal initially, or

$$\hat{\rho}_2(0) = 0. \tag{31}$$

This initial condition is commonly referred to as the assumption of initial random phases. When it applies, eq. (30) makes no reference to the nondiagonal elements of $\hat{\rho}$. Thus the master equation has the desired property of containing only the diagonal elements of $\hat{\rho}$.

When a more general initial condition applies, then all of eq. (30) must be used. Even so, the nondiagonal elements enter only through the initial value $\hat{\rho}_2(0)$. This structure is characteristic of the other master equations, M, PR, and VHS.

If the time dependence of the nondiagonal elements is also of interest, one needs the Laplace inversion of eq. (28). This connects $\hat{\rho}_2(t)$ to $\hat{\rho}_1(t)$.

For the rest of this article we discuss only the diagonal elements, and use only the initial condition $\hat{\rho}_2(0) = 0$.

Explicit form of the master equation. Equation (30) is expressed in an abstract operator notation. Here we change to the more explicit subscript notation. We use the Liouville operator given in eq. (6), and the projection operator given in eq. (23).

At this point we require that the representation be chosen so that the unperturbed energy is diagonal. (This is true of the other master equations too). The unperturbed energy eigenvalues will be denoted by E_n, so that

$$(H_0)_{mn} = E_m\,\delta_{mn}. \tag{32}$$

Then the unperturbed Liouville operator is

$$(L_0)_{mnm'n'} = (E_m - E_n)\,\delta_{mm'}\,\delta_{nn'}. \tag{33}$$

It is a trivial calculation to verify that

$$DL_0 = L_0 D = 0. \tag{34}$$

Also, the product DLD vanishes for any Hamiltonian. This is seen from the definitions, which lead to

$$(DLD)_{mnm'n'} = \delta_{mn}\,L_{mmm'm'}\,\delta_{m'n'}. \tag{35}$$

But because of eq. (6), L_{mmnn} vanishes. Therefore we have

$$DLD = 0. \tag{36}$$

Equation (36) serves to eliminate the first term on the right of eq. (30). The reason is

$$DL\,\hat{\rho}_1 = DLD\,\hat{\rho}. \tag{37}$$

The rest of eq. (30), without the initial value $\hat{\rho}_2(0)$, has the explicit form

$$\frac{\mathrm{d}\hat{\rho}_{mm}(t)}{\mathrm{d}t} = -\int_0^t \mathrm{d}t_1\,[K(t_1)\,\hat{\rho}_1(t-t_1)]_{mm}. \tag{38}$$

We have abbreviated

$$K(t) = DL\,\mathrm{e}^{-it(1-D)L}\,(1-D)L. \tag{39}$$

Because $\hat{\rho}_1$ is diagonal, eq. (38) is

$$\frac{\mathrm{d}\rho_{mm}(t)}{\mathrm{d}t} = -\int_0^t \mathrm{d}t_1 \sum_n K_{mmnn}(t_1)\,\rho_{nn}(t-t_1). \tag{40}$$

As a result of the identities in eq. (34), the memory kernel $K_{mmnn}(t)$ can be simplified slightly to

$$K_{mmnn}(t) = [L_1\,\mathrm{e}^{-it(1-D)L}(1-D)L_1]_{mmnn}. \tag{41}$$

Note that this is formally of the second order in the perturbation; it contains two explicit factors L_1. Higher order dependence on the perturbation comes from the exponential operator in K.

Next we prove the sum rule

$$\sum_n K_{mmnn}(t) = 0. \tag{42}$$

The demonstration starts with

$$\sum_n K_{mmnn} = \sum_n \sum_a \sum_b [L_1\,\mathrm{e}^{-it(1-D)L}(1-D)]_{mmab}\,(L_1)_{abnn} =$$
$$= \{\sum_a \sum_b [L_1\,\mathrm{e}^{-it(1-D)L}(1-D)]_{mmab}\} \times \sum_n (L_1)_{abnn}. \tag{43}$$

But according to the definition of the Liouville operator,

$$\sum_n (L_1)_{abnn} = \sum_n (H_1)_{an}\,\delta_{bn} - \sum_n \delta_{an}\,(H_1)_{nb} \tag{44}$$

which proves our assertion .

The sum rule can be used as follows,

$$\sum_{n \neq m} K_{mmnn} = -K_{nn}, \tag{45}$$

so that our master equation takes the familiar gain-loss form

$$\frac{\mathrm{d}\rho_{mm}(t)}{\mathrm{d}t} = -\int_0^t \mathrm{d}t_1 \sum_{n\neq m} K_{mmnn}(t_1)\,[\rho_{nn}(t-t_1) - \rho_{mm}(t-t_1)] \tag{46}$$

with the kernel K given explicitly by eq. (41).

Montroll's master equation. We demonstrate here the identity of the generalized master equation derived by Montroll [9]) and our own master equation.

Several changes in notation are required to conform with Montroll's work. We replace t_1 by τ, m and n by j and k, and $\hat{H}_1$ by λU.

Montroll's equation has the general structure of eq. (46). To prove the identity of the two equations, we must obtain his memory kernel from ours. We start with the definition of K,

$$K_{jjkk}(\tau) = [L_1\,\mathrm{e}^{-i\tau(1-D)L}\,(1-D)L_1]_{jjkk}. \tag{47}$$

By tetradic multiplication this is

$$= \sum_a \sum_b \sum_c \sum_d (L_1)_{jjab}\,[\mathrm{e}^{-i\tau(1-D)L}]_{abcd}\,(L_1)_{cdkk}. \tag{48}$$

Note that the terminal $(1-D)$ in eq. (47) is redundant, because L_{cckk} always vanishes. For convenience we abbreviate

$$\mathrm{e}^{-i\tau(1-D)L} = \mathscr{G}(\tau). \tag{49}$$

On using the definition of the tetradic L, we obtain

$$K_{jjkk}(\tau) = \lambda^2 \sum_a \sum_b \sum_c \sum_d U_{ba}\,U_{cd}\,\mathscr{G}_{abcd}(\tau) \times \times (\delta_{bj} - \delta_{aj})\,(\delta_{dk} - \delta_{ck}). \tag{50}$$

Montroll's calculation is equivalent to evaluating the elements of the tetradic G by means of Laplace transforms. Let us define

$$\mathscr{D}(p) = \int_0^\infty \mathrm{d}t\,\mathrm{e}^{-pt}\,\mathscr{G}(t). \tag{51}$$

By direct integration this is also

$$\mathscr{D}(p) = \frac{1}{p + i(1-D)L}. \tag{52}$$

We observed earlier in this article that tetradics can be manipulated as if they were matrices, by the device of associating subscript pairs with single integers. Thus the inverse tetradic $\mathscr{D}(p)$ may be calculated in terms of the determinant and minors of the tetradic in the denominator,

$$M = p + i(1-D)L \tag{53}$$

or

$$M_{abcd} = p\,\delta_{ac}\,\delta_{bd}\,\delta_{ab} + i\,\omega_{ab}\,\delta_{ac}\,\delta_{bd} + \\ + i(1-\delta_{ab})\,\{\lambda U_{ac}\,\delta_{bd} - \lambda\,\delta_{ac}\,U_{db}\}. \tag{54}$$

(In writing eq. (54) we used the abbreviation $E_a - E_b = \omega_{ab}$). The determinant of M is $D(p)$. The minor associated with the $[(ab), (cd)]$ element of M is $D(ab/cd; p)$. Thus the inverse is

$$\mathscr{D}_{abcd}(p) = \mathscr{D}(ab/cd; p) = \frac{D(ab/cd; p)}{D(p)}. \tag{55}$$

These quantities are all identical with those introduced by Montroll, and we have used his notation.

Next, we use the operator identity

$$\frac{1}{p+i(1-D)L} = \frac{1}{p+i(1-D)L_0} - \frac{1}{p+i(1-D)L_0}\,i(1-D)L_1\,\frac{1}{p+i(1-D)L} \tag{56}$$

Equation (52) introduces $\mathscr{D}$, and eq. (34) eliminates the quantity DL_0. In this way we obtain

$$\mathscr{D}(p) = \frac{1}{p+iL_0} - \frac{1}{p+iL_0}\,i(1-D)L_1\,\mathscr{D}(p). \tag{57}$$

The unperturbed resolvent, in subscript notation, is

$$\left(\frac{1}{p+iL_0}\right)_{abcd} = \frac{1}{p+i\omega_{ab}}\,\delta_{ac}\,\delta_{bd}, \tag{58}$$

so that

$$\mathscr{D}_{abcd}(p) = \frac{1}{p+i\omega_{ab}}\,\delta_{ac}\,\delta_{bd} - \\ - \frac{i\lambda}{p+i\omega_{ab}}(1-\delta_{ab})\sum_m \{U_{am}\,\mathscr{D}_{mbcd}(p) - U_{mb}\,\mathscr{D}_{amcd}(p)\}. \tag{59}$$

The inverse Laplace transform of eq. (59) is

$$\mathscr{G}_{abcd}(\tau) = e^{-i\omega_{ab}\tau}\,\delta_{ac}\,\delta_{bd} - \\ - \frac{\lambda}{2\pi}\int_{C-i\infty}^{C+i\infty} dp\; e^{p\tau}\,\frac{1-\delta_{ab}}{p+i\omega_{ab}}\sum_m \{U_{am}\mathscr{D}_{mbcd}(p) - U_{mb}\mathscr{D}_{amcd}(p)\}. \tag{60}$$

When this is substituted in eq. (50) to give the kernel $K_{jjkk}(\tau)$, and the kernel is put into eq. (46), we obtain Montroll's form of the master equation.

Prigogine and Résibois' master equation. We demonstrate here the identity of the generalized master equation derived by Prigogine and Résibois and our own master equation.

They use a second-quantized Hamiltonian, in the occupation number representation. This is quite unnecessary, however, and their results are (in a formal sense) considerably more general.

The states of the unperturbed Hamiltonian $\hat{H}_0$ are labelled by the quantum number n. (In the occupation number representation, these are the numbers of elementary excitations in each unperturbed state). We do not have to give any physical interpretation to these quantum numbers. The matrix elements of the unperturbed Hamiltonian are

$$(\hat{H}_0)_{nn'} = E_n \, \delta_{nn'}, \tag{61}$$

and the perturbation $\hat{H}_1 = \lambda V$ has matrix elements $V_{nn'}$.

Résibois uses a special notation for matrix elements. For an arbitrary operator $\hat{A}$, let

$$A_{nn'} = A_{n-n'}\left(\frac{n+n'}{2}\right), \tag{62}$$

and use the abbreviations

$$\nu = n - n'; \; N = \frac{n+n'}{2}. \tag{63}$$

Thus the average of $\hat{A}$ is

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_n \sum_{n'} A_{nn'} \rho_{n'n} = \\ &= \sum_\nu \sum_N A_\nu(N) \, \rho_{-\nu}(N). \end{aligned} \tag{64}$$

When $\hat{A}$ is diagonal in the unperturbed representation, we have

$$\begin{aligned} A_{nn'} &= A_{nn} \, \delta_{nn'}; \\ A_\nu(N) &= A_0(N) \, \delta_{\nu 0}; \end{aligned} \tag{65}$$

so that the average of $\hat{A}$ is

$$\langle \hat{A} \rangle = \sum_N A_0(N) \, \rho_0(N). \tag{66}$$

Thus our master equation is concerned with the N and t dependence of the particular matrix elements $\rho_0(N, t)$.

The Liouville operator is expressed in this notation as follows. We start with

$$L_{mnm'n'} = H_{mm'} \, \delta_{nn'} - \delta_{mm'} \, H_{n'n} \tag{67}$$

and use the substitutions

$$m = N + \frac{\nu}{2}, \quad n = N - \frac{\nu}{2},$$

$$m' = N' + \frac{\nu'}{2}, \quad n' = N' - \frac{\nu'}{2}. \tag{68}$$

Then the Liouville operator is

$$L_{\nu\nu'}(N, N') = H_{\nu-\nu'}(N + \tfrac{1}{2}\nu')\,\delta\left(N' - N - \frac{\nu' - \nu}{2}\right) -$$

$$- H_{\nu-\nu'}(N - \tfrac{1}{2}\nu')\,\delta\left(N' - N + \frac{\nu' - \nu}{2}\right). \tag{69}$$

Following Résibois, we introduce the shift operator $\eta^{\pm\nu}$ which replaces a function of N by the same function of $N \pm \frac{1}{2}\nu$,

$$\eta^{\pm\nu} f(N) = f(N \pm \tfrac{1}{2}\nu). \tag{70}$$

Then the Liouville operator is

$$L_{\nu\nu'}(N, N') = \eta^{\nu'} H_{\nu-\nu'}(N)\,\eta^{-\nu}\,\delta(N - N') -$$

$$- \eta^{-\nu'} H_{\nu-\nu'}(N)\,\eta^{\nu}\,\delta(N - N'). \tag{71}$$

On introducing Résibois' matrix element (still an operator with respect to N),

$$\langle\nu|\mathscr{H}(N)|\nu'\rangle = \eta^{\nu'} H_{\nu-\nu'}(N)\,\eta^{-\nu} - \eta^{-\nu'} H_{\nu-\nu'}(N)\,\eta^{\nu}, \tag{72}$$

we obtain

$$L_{\nu\nu'}(N, N') = \langle\nu|\mathscr{H}(N)|\nu'\rangle\,\delta(N - N'). \tag{73}$$

This representation has the remarkable property of being "diagonal" in N, for the perturbed system as well as the unperturbed one.

The diagonality referred to here is exactly the same as one sees in the coordinate representation of matrix mechanics. For example, the matrix of the momentum operator in the coordinate representation is

$$p(\boldsymbol{r} - \boldsymbol{r}') = -i\nabla_{\boldsymbol{r}}\,\delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{74}$$

This matrix is "diagonal" in the sense that it contains the delta function in positions. As is well known, one can drop the delta function and the matrix notation, and deal exclusively with Schrödinger operators. Résibois does this with respect to the quantum numbers N. Therefore, his operator $\mathscr{H}(N)$ is just another way of writing the Liouville operator L; and his matrix-operator $\langle\nu|\mathscr{H}(N)|\nu'\rangle$ is a matrix with respect to one set of quantum numbers and an operator with respect to the other.

In this notation, von Neumann's equation becomes

$$\frac{\partial \rho_\nu(N,t)}{\partial t} = \sum_{\nu'} \sum_{N'} L_{\nu\nu'}(N,N')\,\rho_{\nu'}(N',t) = \\ = \sum_{\nu'} \langle \nu|\mathscr{H}(N)|\nu'\rangle\,\rho_{\nu'}(N,t). \tag{75}$$

For the moment we keep the full tetradic notation.

The projection operator defined by eq. (23), when rewritten by means of the substitutions in eq. (68), becomes

$$D_{\nu\nu'}(N,N') = \delta(\nu)\,\delta(\nu')\,\delta(N-N'). \tag{76}$$

Note that the projection operator also is diagonal in N.

Now we are ready to go from eq. (38) to the PR master equation. In present notation, eq. (38) is

$$\frac{\mathrm{d}\rho_0(N,t)}{\mathrm{d}t} = -\int_0^t \mathrm{d}t_1 \sum_{N'} K_{00}(N,N';t_1)\,\rho_0(N',t-t_1), \tag{77}$$

and the kernel is

$$K_{00}(N,N';t) = [L_1\,\mathrm{e}^{-it(1-D)L}\,(1-D)\,L_1]_{00,NN'}. \tag{78}$$

For simplicity of notation we have written the (N,N') dependence as subscripts.

Each tetradic in the kernel contains a delta function in N; see eqs. (73) and (76). Now we drop these delta functions and deal exclusively with *operators* in N space. The tetradic $L_{\nu\nu'}(N,N)$ is replaced by the matrix-operator $\langle\nu|\mathscr{H}(N)|\nu'\rangle$, and the projection operator tetradic $D_{\nu\nu'}(N,N')$ is replaced by the matrix

$$\langle\nu|\mathscr{D}|\nu'\rangle = \delta(\nu)\,\delta(\nu'). \tag{79}$$

The operator corresponding to the matrix $K_{00}(N,N';t)$ will be denoted by $-G(N,t)$. Evidently its explicit formula is

$$-G(N,t) = \langle 0|\,\mathscr{H}_1\,\mathrm{e}^{-it(1-\mathscr{D})\mathscr{H}}\,(1-\mathscr{D})\mathscr{H}_1\,|0\rangle, \tag{80}$$

where $\langle 0|\,-\,|0\rangle$ means the matrix element between $\nu=0$ and $\nu=0$. The N dependence of $\mathscr{H}$ was left implicit to save space.

In this operator notation, eq. (77) is

$$\frac{\mathrm{d}\rho_0(N,t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t_1\,G(N,t_1)\,\rho_0(N,t-t_1). \tag{81}$$

This has precisely the form of PR. All that remains is to show the identity of G, as defined in eq. (80), with the quantity G_{00} defined by Résibois.

By means of residue theory, we may express G in terms of a new quantity $\psi(Z)$,

$$G(N, t) = \frac{1}{2\pi i} \oint \mathrm{d}z\, \mathrm{e}^{-itz} \psi(Z) \tag{82}$$

where $\psi(Z)$ must have the value

$$\psi(Z) = -\left\langle 0 \left| \mathscr{H}_1 \frac{1}{Z - (1-\mathscr{D})\mathscr{H}} (1-\mathscr{D})\, \mathscr{H}_1 \right| 0 \right\rangle. \tag{83}$$

The Hamiltonian is separated into two parts, the unperturbed $\hat{H}_0$ and the perturbation $\hat{H}_1 = \lambda V$; the Liouville operator $\mathscr{H}$ is separated in just the same way into $\mathscr{H}_0$ and $\mathscr{H}_1 = \lambda\mathscr{V}$,

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \lambda V, \\ \mathscr{H} &= \mathscr{H}_0 + \lambda\mathscr{V}. \end{aligned} \tag{84}$$

Now we make the familiar power series expansion

$$\begin{aligned} \frac{1}{Z-(1-\mathscr{D})\mathscr{H}} = \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} + \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} (1-\mathscr{D})\lambda\mathscr{V} \cdot \\ \cdot \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} + \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} (1-\mathscr{D})\lambda\mathscr{V} \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} (1-\mathscr{D})\lambda\mathscr{V} \cdot \\ \cdot \frac{1}{Z-(1-\mathscr{D})\mathscr{H}_0} + \ldots. \end{aligned} \tag{85}$$

Because DL_0 vanishes, as in eq. (34), it is obvious that $\mathscr{D}\mathscr{H}_0$ also vanishes and that

$$Z - (1 - \mathscr{D})\mathscr{H}_0 = Z - \mathscr{H}_0. \tag{86}$$

Then the expansion of $\psi(Z)$ is

$$\begin{aligned} \psi(Z) = -\left\langle 0 \left| \lambda\mathscr{V} \left\{ \frac{1}{Z-\mathscr{H}_0} + \frac{1}{Z-\mathscr{H}_0} (1-\mathscr{D})\, \lambda\mathscr{V} \frac{1}{Z-\mathscr{H}_0} + \right.\right.\right. \\ \left.\left.\left. + \frac{1}{Z-\mathscr{H}_0} (1-\mathscr{D})\, \lambda\mathscr{V} \frac{1}{Z-\mathscr{H}_0} (1-\mathscr{D})\, \lambda\mathscr{V} \frac{1}{Z-\mathscr{H}_0} + \ldots \right\} (1-\mathscr{D})\, \lambda\mathscr{V} \right| 0 \right\rangle. \end{aligned} \tag{87}$$

The projection operators $1 - \mathscr{D}$ contained in each term have the effect that in calculating matrix products, no intermediate states with $\nu = 0$ may occur. This is the same as the irreducibility criterion of Résibois. We drop the $1 - \mathscr{D}$ and instead put a subscript $\nu \neq 0$ on the matrix elements,

$$\psi(Z) = -\left\langle 0 \left| \lambda\mathscr{V} \left\{ \frac{1}{Z-\mathscr{H}_0} + \frac{1}{Z-\mathscr{H}_0} \lambda\mathscr{V} \frac{1}{Z-\mathscr{H}_0} + \ldots \right\} \lambda\mathscr{V} \right| 0 \right\rangle_{\nu\neq 0}. \tag{88}$$

But this is precisely the formula given by Résibois [8]) for his operator $\psi_{00}^{+}(Z)$. We conclude that our $G(N, t)$ is identical with his $G_{00}(N, t)$. Thus the master equations PR and NZ are identical.

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