Liouville space theory of sequential quantum processes. I. General theory

1982 J. Phys. A: Math. Gen. 15 2157

(http://iopscience.iop.org/0305-4470/15/7/026)

J. Phys. A: Math. Gen. 15 (1982) 2157–2176. Printed in Great Britain

Liouville space theory of sequential quantum processes: I. General theory

B J Dalton

Physics Department, University of Queensland, St Lucia, Brisbane, Queensland 4067, Australia

Received 4 August 1981, in final form 21 January 1982

Abstract. The theory of sequential quantum processes has been extended to Liouville space via the use of non-Hermitian projection operators in order to treat the evolution of the quantum density operator and to enable physically important matrix elements of the density operator to be calculated. The formal relationship of master equation methods to the theory of sequential quantum processes is established, and a new set of coupled master equations is derived. Special choices of projection operators lead to further simplification of the results. The Markoff approximation is also examined.

1. Introduction

Determination of the time development of the quantum density operator $\rho(t)$ is fundamental to many applications in non-equilibrium statistical physics in which the system is not in a pure quantum state.

In most cases not all density operator matrix elements are of equal interest, often it is only necessary to calculate certain elements or sums of elements. For example, if the quantum system consists of a small system S interacting with a large system R (or reservoir), it is well known (see Cohen-Tannoudji 1977, Agarwal 1974, Haake 1973) that it is usually only important to determine the so-called reduced density operator $\sigma^{S}(t)=\mathrm{Tr}_{R}\rho(t)$ or in terms of matrix elements

$$\sigma^{S}_{ij}(t)=\sum_{A}\rho_{iA;jA}(t) \tag{1}$$

where i,j refer to states of the small system S and A refers to the states of the reservoir R. A second example is where it is of interest to consider the diagonal density matrix elements in order to set up generalised rate equations for the populations of the states $|i\rangle$ of a quantum system (Agarwal 1973, Zwanzig 1961, 1964). A third example is treated in the following paper, where a system consisting of discrete states $|i\rangle$ and continuum states $|\alpha\rangle$ is considered. The continuum states may in certain circumstances constitute a so-called internal reservoir (contrasting the first example where the separate quantum system R is an external reservoir) in that discrete to continuum transitions may be essentially irreversible. Three different types of density matrix element ρ_{ij}, $\rho_{\alpha i}(=\rho^{*}_{i\alpha})$ and $\rho_{\alpha\beta}$ can be distinguished, of which the elements ρ_{ij} (giving the populations and coherences of the discrete states) and $\rho_{\alpha\alpha}$ (giving the populations of the continuum states) are usually of most interest. This third example applies to problems such as atomic autoionisation and resonant multiphoton ionisation (ignoring spontaneous emission processes). A fourth example is an extension of the third, in which it is desirable to divide the discrete states into resonant and virtual states according to whether transitions from the initial state are approximately energy conserving or not. Six different types of density matrix element would then be involved. This case applies to multiphoton processes involving both resonant and non-resonant steps. Examples involving combinations of the above situations also occur. For example, a combination of the first and third cases applies in the theory of resonant multiphoton ionisation allowing for spontaneous emission processes (Dalton 1982), in which the states of the unoccupied radiation field modes act as an external reservoir and products of atomic continuum states with n-photon states of the exciting laser mode act as the internal reservoir. The photoelectron spectrum involves diagonal density matrix elements for the latter product states. The spontaneous emission spectrum can be obtained from the equations (master equations) governing density matrix elements between states which are products of atomic discrete states and n-photon states of the exciting laser mode.

It is clearly desirable to develop methods for calculating separately the part or parts of $\rho(t)$ of most relevance to the problem being studied without having to obtain a complete expression for $\rho(t)$.

One such approach is that of master equations (see, for example, Zwanzig 1961, Agarwal 1973, Haake 1973), in which the relevant part of $\rho(t)$ satisfies, in general, integro-differential equations, although so far this approach seems to have been applied only to the case where the density matrix elements are divided up into a single set of relevant elements (for example, diagonal elements) and the remaining non-relevant elements (for example, off-diagonal elements). Another approach which is developed in this paper, is to extend the theory of sequential quantum processes to apply to the evolution of $\rho(t)$. This theory was designed by Mower (1968) and extended by Cresser and Dalton (1980), to treat processes describable in the ordinary state space of the Schrödinger state vector $|\psi(t)\rangle$.

The theory of sequential quantum processes and the master equation approach (as extended here) are in fact equivalent to each other, being related via Laplace transformations. This result will be shown in § 3 where sets of coupled master equations for the various parts of ρ are derived from the sequential quantum processes results. An example of the coupled master equations occurs in the case of the system with an internal reservoir (example three above) where the special result, equation (42), applies. The coupled master equations (i) relate $\dot{\rho}_{ij}$ to various ρ_{kl} (at earlier times) (ii) relate $\dot{\rho}_{\alpha i}$ (and $\dot{\rho}_{i\alpha}$) to various ρ_{kl} (at earlier times) and (iii) relate $\dot{\rho}_{\alpha\beta}$ to various $\rho_{\gamma i}$ (and $\rho_{i\gamma}$) (at earlier times). Applied to the specific problem of resonant multiphoton ionisation, the equations for $\dot{\rho}_{\alpha\alpha}$ could be used to develop expressions for the photoelectron spectrum, those for $\dot{\rho}_{ij}$ could be used to develop expressions for the time-dependent ionisation probability (see Dalton 1982).

Having demonstrated the important result that the theory of sequential quantum processes and the coupled master equations are formally equivalent, the question then arises as to their relative utility. This depends on the particular application, but often situations leading to a simplification of the one also lead to a simplification of the other. For example, master equations become simpler when the Markoff approximation can be made, which occurs when the relevant matrix elements of certain relaxation operators (see equation (22) below) behave essentially like Dirac delta functions. However, in this case the corresponding matrix elements of certain line shift operators (see equation (18) below) are essentially independent of the Laplace variable z, in which case the pole approximation can be made, leading to a simplification of sequential quantum processes results. In the Markovian case, master equations are a convenient starting point to obtain steady-state solutions (by putting the time derivatives equal to zero) and in quantum optics applications lead to the important optical Bloch equations, thereby enabling analogies to be drawn with work on nuclear spin resonance. However, in the general non-Markovian case, the most practical method of solving the coupled master equations would be via Laplace transforms, which of course then yields the sequential quantum processes results.

The treatment given here involves resolvent operator theory in Liouville space and makes use of non-Hermitian projection operators in general. The relevant parts of $\rho(t)$ are given as Laplace transform expressions for the quantities $\Lambda_i|\rho(t)\rangle\!\rangle$ (see equation (11)) in terms of results for projections of the resolvent operator, $\Lambda_i\mathscr{G}(z)\Lambda_0$ (see equation (20)). The latter expression in turn involves line shift operators $\mathscr{R}^i(z)$ acting in Liouville space (see equations (18), (19)). The results, which are derived in § 2, are formally identical to those for state space. A new set of related coupled master equations for the $\Lambda_i|\rho\rangle\!\rangle$ is then derived in § 3. The results obtained (see equations (28), (37)) are exact, but may in certain cases be treated via the standard Markoff approximation approach (§ 5). Further simplifications to the results can be obtained (see § 4) when the interaction contribution to the Liouville operator satisfies certain conditions. These simplifications are analogous to those discussed earlier for state space (Cresser and Dalton 1980), but the conditions on the interaction Liouville operator are not in general equivalent to those applying in Cresser and Dalton (1980).

An illustrative application of the results for the case of a system with an internal reservoir is presented in the following paper (to be referred to as paper II).

2. Resolvent operator theory of sequential quantum processes

In the notation of Liouville space (see appendix 1) the quantum density operator $\rho(t)$ is represented by a vector $|\rho(t)\rangle\!\rangle$ satisfying the Liouville equation

$$i\hbar\frac{d}{dt}|\rho\rangle\!\rangle=\mathscr{L}|\rho\rangle\!\rangle \tag{2}$$

where $\mathscr{L}$ is the Liouville operator, related to the time-independent Hamiltonian H for the system via

$$\mathscr{L}=H\times 1-1\times H. \tag{3}$$

The Liouville equation can be solved, analogously to the time-dependent Schrödinger equation (the latter case is discussed by Goldberger and Watson (1964), Mower (1966, 1968), Cresser and Dalton (1980)), via Laplace transform methods in terms of a resolvent operator $\mathscr{G}(z)=(z-\mathscr{L})^{-1}$ acting in Liouville space (Zwanzig 1961, 1964, Haake 1973, Agarwal 1973, 1974). Thus

$$|\rho(t)\rangle\!\rangle=\frac{\hbar}{2\pi i}\int_c d\omega\ e^{-i\omega t}\mathscr{G}(\hbar\omega)|\rho(0)\rangle\!\rangle \qquad t\geqslant 0 \tag{4}$$

where c is the contour just above the real axis in the complex ω plane that goes from $+\infty$ to $-\infty$, and where the quantum density operator at $t=0$ is $\rho(0)$.

As discussed in the introduction, it is often only necessary to calculate certain density matrix elements or sums of elements. A convenient method of setting up equations for the various parts of ρ is to make use of projection operators (projectors), a technique introduced by Zwanzig (1961).

We consider then a set of projection operators acting in Liouville space $\Lambda_0, \Lambda_1, \Lambda_2, \ldots, \Lambda_i, \ldots$, which are such that

$$\Lambda_i^2 = \Lambda_i \tag{5a}$$

$$\Lambda_i \Lambda_j = \Lambda_j \Lambda_i = 0 \qquad i \neq j. \tag{5b}$$

Associated projectors $Q_0, Q_1, Q_2, \ldots, Q_i, \ldots$ are introduced via (1 is the unit operator in Liouville space)

$$\begin{aligned} Q_0 &= 1 - \Lambda_0 \\ Q_1 &= 1 - \Lambda_0 - \Lambda_1 \\ &\vdots \\ Q_i &= 1 - \sum_{j=0}^{i} \Lambda_i. \end{aligned} \tag{6}$$

These associated projectors therefore satisfy

$$Q_i = Q_{i-1} - \Lambda_i \tag{7a}$$

$$Q_j = \Lambda_{j+1} + \Lambda_{j+2} + \ldots + \Lambda_i + Q_i \qquad i > j \tag{7b}$$

$$\Lambda_i Q_i = Q_i \Lambda_i = 0 \tag{7c}$$

$$\Lambda_i Q_j = Q_j \Lambda_i = 0 \qquad i < j \tag{7d}$$

$$\Lambda_i Q_j = Q_j \Lambda_i = \Lambda_i \qquad i > j \tag{7e}$$

$$Q_i^2 = Q_i \tag{7f}$$

$$Q_i Q_j = Q_i \qquad i > j \tag{7g}$$

$$Q_i Q_j = Q_j \qquad i < j. \tag{7h}$$

The projector Λ_0 is chosen so as to leave the initial density operator $|\rho(0)\rangle\rangle$ unchanged, whilst the remaining projectors are chosen so as to yield zero when applied to $|\rho(0)\rangle\rangle$

$$\Lambda_0 |\rho(0)\rangle\rangle = |\rho(0)\rangle\rangle \tag{8a}$$

$$\Lambda_i |\rho(0)\rangle\rangle = 0 \qquad i \geqslant 1. \tag{8b}$$

Finally, in the applications of interest, the Hamiltonian H can be written as the sum, $K + V$, of an unperturbed Hamiltonian K and an interaction V which causes transitions to occur between the eigenstates of K. The Liouville operator $\mathscr{L}$ can then be written

$$\mathscr{L} = \mathscr{K} + \mathscr{V} \tag{9a}$$

where

$$\mathscr{K} = K \times 1 - 1 \times K \tag{9b}$$

$$\mathscr{V} = V \times 1 - 1 \times V. \tag{9c}$$

The projectors Λ_i are also chosen so as to satisfy

$$\Lambda_i\mathscr{K}=\mathscr{K}\Lambda_i \tag{10a}$$

and hence also from equation (6)

$$Q_i\mathscr{K}=\mathscr{K}Q_i. \tag{10b}$$

The physically important matrix elements of $\rho(t)$ are determined from $\Lambda_i|\rho(t)\rangle\!\rangle$ $(i=0,1,2,\ldots)$. Using equations (4) and (8*a*) we obtain

$$\Lambda_i|\rho(t)\rangle\!\rangle=\frac{\hbar}{2\pi\mathrm{i}}\int_c \mathrm{d}\omega\ \mathrm{e}^{-\mathrm{i}\omega t}\Lambda_i\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle \qquad t\geqslant 0 \qquad i=0,1,2,\ldots. \tag{11}$$

Analogous to the theory of sequential quantum processes in the usual vector space of state vectors $|\psi(t)\rangle$ (Mower 1966, 1968, Cresser and Dalton 1980) a determination of expressions of the form $\Lambda_i\mathscr{G}(\hbar\omega)\Lambda_0$ would hopefully display all the important ω variations, enabling the contour integral in equation (11) to be calculated. This theory of sequential quantum processes in Liouville space is outlined in this section.

Before developing the general theory, examples of projectors should be given. For the first example of a small quantum system S interacting with a large reservoir R, it is convenient to introduce the projector (a similar projector was first used by Argyres and Kelley (1964), their projector is equivalent to Q_0) Λ_0 defined by

$$\Lambda_0=|\sigma^{\mathrm{R}}(0)\rangle\!\rangle\langle\!\langle 1_{\mathrm{R}}|1_{\mathrm{S}} \tag{12}$$

where it is assumed that at $t=0$ the density operator factorises as a product of the initial density operator $\sigma^{\mathrm{R}}(0)$ for the reservoir and an initial density operator $\sigma^{\mathrm{S}}(0)$ for the small system S. Thus

$$|\rho(0)\rangle\!\rangle=\underset{\begin{pmatrix}\text{vector in}\\ \text{R-Liouville}\\ \text{space}\end{pmatrix}}{|\sigma^{\mathrm{R}}(0)\rangle\!\rangle}\ \underset{\begin{pmatrix}\text{vector in}\\ \text{S-Liouville}\\ \text{space}\end{pmatrix}}{|\sigma^{\mathrm{S}}(0)\rangle\!\rangle}. \tag{13}$$

In equation (12) $|1_{\mathrm{R}}\rangle\!\rangle$ is the vector in R-Liouville space that represents the ordinary unit operator and 1_{S} is the unit operator in S-Liouville space.

In terms of Λ_0 we have

$$\begin{aligned}\Lambda_0|\rho(t)\rangle\!\rangle&=|\sigma^{\mathrm{R}}(0)\rangle\!\rangle\langle\!\langle 1_{\mathrm{R}}|\rho(t)\rangle\!\rangle\\ &=|\sigma^{\mathrm{R}}(0)\rangle\!\rangle|\mathrm{Tr}_{\mathrm{R}}\rho(t)\rangle\!\rangle\\ &=|\sigma^{\mathrm{R}}(0)\rangle\!\rangle|\sigma^{\mathrm{S}}(t)\rangle\!\rangle.\end{aligned} \tag{14}$$

Putting $t=0$ shows that equation (8*a*) is satisfied. Hence the S-Liouville space vector representing the reduced density operator can be obtained via equation (15), which is equivalent to equation (1)

$$|\sigma^{\mathrm{S}}(t)\rangle\!\rangle=\langle\!\langle 1_{\mathrm{R}}|\Lambda_0|\rho(t)\rangle\!\rangle. \tag{15}$$

For this system the unperturbed Hamiltonian K is of the form $H_{\mathrm{S}}+H_{\mathrm{R}}$, where H_{S} is the Hamiltonian of the small system S and H_{R} is the Hamiltonian of the reservoir. It is also assumed that the reservoir is in steady state at $t=0$ and hence $[H_{\mathrm{R}},\sigma_{\mathrm{R}}(0)]=0$. From these assumptions we can show that $\Lambda_0^2=\Lambda_0$ and $\Lambda_0\mathscr{K}=\mathscr{K}\Lambda_0$, as required by the general theory. This projector Λ_0 has been used extensively (see Agarwal 1974, Haake 1973, Cohen-Tannoudji 1975). The above properties are derived in Cohen-Tannoudji (1975). The projector Λ_1 can be chosen equal to Q_0 and hence $Q_1=0$.

In this example the projector Λ_0 is non-Hermitian, but fortunately the development of the theory of sequential quantum processes in Liouville space and the derivation of the master equations does not depend on this, although they are Hermitian in some applications. In general then, the Λ_i cannot be written in the form

$$\sum_{\lambda\mu} |\lambda\mu^\dagger\rangle\!\rangle\langle\!\langle\lambda\mu^\dagger|$$

where $|\lambda\rangle$, $|\mu\rangle$ are a suitable orthonormal basis set for the quantum system.

For the second example discussed in the introduction, and where $\rho(0)$ contains no off-diagonal elements, it is convenient to introduce

$$\begin{aligned} \Lambda_0 &= \sum_i |ii^\dagger\rangle\!\rangle\langle\!\langle ii^\dagger| \qquad & Q_0 &= \Lambda_1 \\ \Lambda_1 &= \sum_{i\neq j} |ij^\dagger\rangle\!\rangle\langle\!\langle ij^\dagger| \qquad & Q_1 &= 0. \end{aligned} \tag{16}$$

In this case $\Lambda_0|\rho\rangle\!\rangle$ will only involve diagonal density matrix elements ρ_{ii}, whereas $\Lambda_1|\rho\rangle\!\rangle$ will only contain off-diagonal elements..

For the third example discussed in the introduction and where $\rho(0)$ only involves matrix elements $\rho_{ij}(0)$ it is convenient to introduce (see paper II for details)

$$\begin{aligned} \Lambda_0 &= \sum_{ij} |ij^\dagger\rangle\!\rangle\langle\!\langle ij^\dagger| \qquad & Q_0 &= \Lambda_1+\Lambda_2 \\ \Lambda_1 &= \sum_{\alpha i} (|i\alpha^\dagger\rangle\!\rangle\langle\!\langle i\alpha^\dagger| + |\alpha i^\dagger\rangle\!\rangle\langle\!\langle \alpha i^\dagger|) \qquad & Q_1 &= \Lambda_2 \\ \Lambda_2 &= \sum_{\alpha\beta} |\alpha\beta^\dagger\rangle\!\rangle\langle\!\langle\alpha\beta^\dagger| \qquad & Q_2 &= 0. \end{aligned} \tag{17}$$

In this case $\Lambda_0|\rho\rangle\!\rangle$, $\Lambda_1|\rho\rangle\!\rangle$ and $\Lambda_2|\rho\rangle\!\rangle$ will involve density matrix elements ρ_{ij}, $\rho_{\alpha i}$ (and $\rho_{i\alpha}$), $\rho_{\alpha\beta}$ respectively, so that the discrete-state coherences and populations will be obtained from $\Lambda_0|\rho\rangle\!\rangle$, whilst the continuum-state populations will be obtained from $\Lambda_2|\rho\rangle\!\rangle$. The form of $\mathscr{H}$ compatible with equation (10a) is discussed in the accompanying paper.

Analogous to the previous work (Mower 1968, Cresser and Dalton 1980) on sequential quantum processes, we can introduce line shift operators $\mathscr{R}^i(z)$ and reduced resolvent operators $\Lambda_i\mathscr{G}^i(z)\Lambda_i$, which are now of course operators in Liouville space. They are defined by

$$\mathscr{R}^i(z) = \mathscr{V} + \mathscr{V}Q_i(z - Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V} \tag{18}$$

and

$$\Lambda_i\mathscr{G}^i(z)\Lambda_i = \Lambda_i[z - \mathscr{H} - \Lambda_i\mathscr{R}^i(z)\Lambda_i]^{-1}\Lambda_i. \tag{19}$$

The operators $\mathscr{R}^i(z)$ will be referred to as line shift operators rather than as level shift operators as in the case of ordinary state space, since they will determine shifts and widths of spectral transition frequencies rather than of energy levels.

Methods similar to those in Mower (1966, 1968) and Cresser and Dalton (1980) can be used to obtain expressions for $\Lambda_0\mathscr{G}(z)\Lambda_0$ and $\Lambda_i\mathscr{G}(z)\Lambda_0$ $(i \geq 1)$. The treatment is not quite the same as the previous work which is partially written as if the projectors were Hermitian, for example they are said to span certain vector subspaces. The final results obtained here only depend on the properties given in equations (5), (7) and (10). The derivation is carried out for completeness in appendix 2.

It is found that

$$\Lambda_0\mathscr{G}(z)\Lambda_0=\Lambda_0\mathscr{G}^0(z)\Lambda_0 \tag{20a}$$

$$\Lambda_i\mathscr{G}(z)\Lambda_0=\sum_{\substack{\text{paths}\\ \{i,j,\ldots,0\}}}\Lambda_i\mathscr{G}^i(z)\Lambda_i\Lambda_i\mathscr{R}^i(z)\Lambda_j\Lambda_j\mathscr{G}^j(z)\Lambda_j\Lambda_j\mathscr{R}^j(z)\ldots\Lambda_0\mathscr{G}^0(z)\Lambda_0 \qquad i\geqslant 1 \tag{20b}$$

where a path from 0 to i is specified by a sequence of numbers $i, j, k, \ldots, 0$ such that $i>j>k>\ldots>0$.

As part of the derivation an important identity for the line shift operators is established

$$\mathscr{R}^{i-1}(z)=\mathscr{R}^i(z)+\mathscr{R}^i(z)\Lambda_i\mathscr{G}^i(z)\Lambda_i\mathscr{R}^i(z) \qquad i\geqslant 1. \tag{21}$$

The equations (20) are the basic results in the theory of sequential quantum processes.

3. Derivation of master equations

We now make use of the formal expressions for the $\Lambda_i\mathscr{G}(\hbar\omega)\Lambda_0$ to obtain a set of coupled master equations for the $\Lambda_i|\rho\rangle\!\rangle$.

In determining master equations we introduce relaxation operators $R^i(\tau)$ $(\tau\geqslant 0)$ in terms of Laplace transforms of the line shift operators $\mathscr{R}^i(\hbar\omega)$. Thus for all $i=0, 1, 2, \ldots$

$$R^i(\tau)=-\frac{1}{2\pi}\int_c \mathrm{d}\omega\ \mathrm{e}^{-\mathrm{i}\omega\tau}\mathscr{R}^i(\hbar\omega) \qquad \tau\geqslant 0 \tag{22a}$$

$$\mathscr{R}^i(\hbar\omega)=\int_0^\infty \mathrm{d}\tau\ \mathrm{e}^{\mathrm{i}\omega\tau}R^i(\tau) \qquad \operatorname{Im}\omega>0. \tag{22b}$$

The Laplace transform expressions used here follow those of Goldberger and Watson (1964), rather than the usual expressions (Morse and Feshbach 1953).

Thus (LT = Laplace transform)

$$\mathscr{R}^i(\hbar\omega)=\mathrm{i}\times[\mathrm{LT}\,R^i(\tau)]. \tag{22c}$$

3.1. Master equation for $\Lambda_0|\rho\rangle\!\rangle$

From equations (11) and (20*a*) we see that

$$\begin{aligned}\mathrm{LT}(\Lambda_0|\rho\rangle\!\rangle)&=\hbar\Lambda_0\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle\\ &=\hbar\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle.\end{aligned} \tag{23}$$

Thus using the result for the Laplace transform of a derivative (Morse and Feshbach 1953) and equation (23) we have

$$\mathrm{LT}\left(\frac{\mathrm{d}}{\mathrm{d}t}(\Lambda_0|\rho\rangle\rangle)\right) = -\frac{1}{\mathrm{i}}\Lambda_0|\rho(0)\rangle\rangle + \frac{\omega}{\mathrm{i}}[\mathrm{LT}(\Lambda_0|\rho\rangle\rangle)] \tag{24}$$

$$= \frac{1}{\mathrm{i}}(-\Lambda_0 + \hbar\omega\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0)|\rho(0)\rangle\rangle$$

$$= \frac{1}{\mathrm{i}}[-\Lambda_0(\hbar\omega - \Lambda_0\mathscr{H}\Lambda_0 - \Lambda_0\mathscr{R}^0(\hbar\omega)\Lambda_0)\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0$$

$$+ \hbar\omega\Lambda_0\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0]|\rho(0)\rangle\rangle.$$

In deriving the last equation we have also used a result obtained similarly to equations (A2.11), (A2.13):

$$\Lambda_0 = \Lambda_0(z - \Lambda_0\mathscr{H}\Lambda_0 - \Lambda_0\mathscr{R}^0(z)\Lambda_0)\Lambda_0\mathscr{G}^0(z)\Lambda_0. \tag{25}$$

Thus using equations (23), (22)

$$\mathrm{LT}\frac{\mathrm{d}}{\mathrm{d}t}(\Lambda_0|\rho\rangle\rangle)$$

$$= \frac{1}{\mathrm{i}}\Lambda_0\mathscr{H}\Lambda_0\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|\rho(0)\rangle\rangle + \frac{1}{\mathrm{i}}\Lambda_0\mathscr{R}^0(\hbar\omega)\Lambda_0\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|\rho(0)\rangle\rangle$$

$$= \frac{1}{\mathrm{i}\hbar}\Lambda_0\mathscr{H}\Lambda_0 \times [\mathrm{LT}(\Lambda_0|\rho\rangle\rangle)] + \frac{1}{\mathrm{i}\hbar}\Lambda_0\mathscr{R}^0(\hbar\omega)\Lambda_0 \times [\mathrm{LT}(\Lambda_0|\rho\rangle\rangle)] \tag{26}$$

$$= \frac{1}{\mathrm{i}\hbar}\Lambda_0\mathscr{H}\Lambda_0 \times [\mathrm{LT}(\Lambda_0|\rho\rangle\rangle)] + \frac{1}{\mathrm{i}\hbar}\mathrm{i}[\mathrm{LT}(\Lambda_0 \boldsymbol{R}^0\Lambda_0)] \times [\mathrm{LT}(\Lambda_0|\rho\rangle\rangle)]. \tag{27}$$

Hence using the convolution theorem for Laplace transforms (Morse and Feshbach 1953) we obtain the master equation for $\Lambda_0|\rho\rangle\rangle$

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_0|\rho(t)\rangle\rangle = \Lambda_0\mathscr{H}\Lambda_0\Lambda_0|\rho(t)\rangle\rangle + \int_0^t \mathrm{d}\tau\,\Lambda_0\boldsymbol{R}^0(\tau)\Lambda_0\Lambda_0|\rho(t-\tau)\rangle\rangle. \tag{28}$$

This equation is equivalent to the well known Zwanzig–Nakajima equation (Zwanzig 1961, Nakajima 1958). A similar equation is given by Cohen-Tannoudji (1975), (equation (9.17)) but in terms of quantities defined via Fourier transforms.

3.2. Master equation for $\Lambda_i|\rho\rangle\rangle$ $(i \geq 1)$

From equation (11) we see that

$$\mathrm{LT}(\Lambda_i|\rho\rangle\rangle) = \hbar\Lambda_i\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\rangle. \tag{29}$$

Using equation (20*b*) we have

$$\Lambda_i\mathscr{G}(\hbar\omega)\Lambda_0 = \Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i \sum_{\substack{\text{paths}\\ j<i\\ \{j,\ldots,0\}}} \Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}^j(\hbar\omega)\Lambda_j\Lambda_j\mathscr{R}^j(\hbar\omega)\ldots\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0$$

$$= \Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0. \tag{30}$$

Hence we find that

$$\mathrm{LT}\,(\Lambda_i|\rho\rangle\!\rangle)=\hbar\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle. \tag{31}$$

Then using equations (30), (31) and (8*b*) and an equation analogous to (24) we have

$$\mathrm{LT}\frac{\mathrm{d}}{\mathrm{d}t}(\Lambda_i|\rho\rangle\!\rangle)$$

$$=-\frac{1}{\mathrm{i}}\Lambda_i|\rho(0)\rangle\!\rangle+\frac{\omega}{\mathrm{i}}[\mathrm{LT}\,(\Lambda_i|\rho\rangle\!\rangle)] \tag{32}$$

$$=\frac{1}{\mathrm{i}}\hbar\omega\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$=\frac{1}{\mathrm{i}}[\Lambda_i(\hbar\omega-\Lambda_i\mathscr{H}\Lambda_i-\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_i)+\Lambda_i\mathscr{H}\Lambda_i+\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_i]$$

$$\times\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$=\frac{1}{\mathrm{i}}\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$+\frac{1}{\mathrm{i}}\Lambda_i\mathscr{H}\Lambda_i\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$+\frac{1}{\mathrm{i}}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_i\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle. \tag{33}$$

In deriving equation (33) we have also used a result obtained similarly to equations (2.11), (2.13)

$$\Lambda_i=\Lambda_i(z-\Lambda_i\mathscr{H}\Lambda_i-\Lambda_i\mathscr{R}^i(z)\Lambda_i)\Lambda_i\mathscr{G}^i(z)\Lambda_i. \tag{34}$$

Collecting terms and using equations (21), (22), (29) and (31), we have

$$\mathrm{LT}\frac{\mathrm{d}}{\mathrm{d}t}(\Lambda_i|\rho\rangle\!\rangle)$$

$$=\frac{1}{\mathrm{i}}\Lambda_i[\mathscr{R}^i(\hbar\omega)+\mathscr{R}^i(\hbar\omega)\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\mathscr{R}^i(\hbar\omega)]\sum_{j<i}\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$+\frac{1}{\mathrm{i}}\Lambda_i\mathscr{H}\Lambda_i\Lambda_i\mathscr{G}^i(\hbar\omega)\Lambda_i\sum_{j<i}\Lambda_i\mathscr{R}^i(\hbar\omega)\Lambda_j\Lambda_j\mathscr{G}(\hbar\omega)\Lambda_0|\rho(0)\rangle\!\rangle$$

$$=\frac{1}{\mathrm{i}\hbar}\Lambda_i\mathscr{H}\Lambda_i\times[\mathrm{LT}\,(\Lambda_i|\rho\rangle\!\rangle)]+\frac{1}{\mathrm{i}\hbar}\Lambda_i\mathscr{R}^{i-1}(\hbar\omega)\sum_{j<i}[\mathrm{LT}(\Lambda_j|\rho\rangle\!\rangle)] \tag{35}$$

$$=\frac{1}{\mathrm{i}\hbar}\Lambda_i\mathscr{H}\Lambda_i\times[\mathrm{LT}\,(\Lambda_i|\rho\rangle\!\rangle)]+\frac{1}{\mathrm{i}\hbar}\mathrm{i}\sum_{j<i}[\mathrm{LT}(\Lambda_i\boldsymbol{R}^{i-1}\Lambda_j)]\times[\mathrm{LT}\,(\Lambda_j|\rho\rangle\!\rangle)]. \tag{36}$$

Thus, from the convolution theorem for Laplace transforms (Morse and Feshbach 1953), we obtain the master equations for $\Lambda_i|\rho\rangle\!\rangle$ $(i\geqslant 1)$

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_i|\rho(t)\rangle\!\rangle=\Lambda_i\mathscr{H}\Lambda_i\Lambda_i|\rho(t)\rangle\!\rangle+\sum_{j<i}\int_0^t\mathrm{d}t\,\Lambda_i\boldsymbol{R}^{i-1}(\tau)\Lambda_j\Lambda_j|\rho(t-\tau)\rangle\!\rangle. \tag{37}$$

These equations together with equation (28) will form a coupled set of master equations in the form of integro-differential equations, and which are exact. In the case where the Markoff approximation can be applied they simplify to differential equations. In all cases the set of master equations is equivalent to the set of equations for the $\Lambda_i\mathcal{G}\Lambda_0$ $(i=0, 1, \ldots)$ given in equation (20). Indeed the expressions for $\Lambda_i\mathcal{G}(\hbar\omega)\Lambda_0$ would constitute the Laplace transform solutions of the master equations.

4. Simplifications associated with conditions on $\mathcal{V}$

4.1. *Case A*

In this case the Λ_i are such that for $j<i$

$$\Lambda_i\mathcal{V}\Lambda_j=0 \qquad j<i-1 \tag{38a}$$

$$Q_i\mathcal{V}\Lambda_j=0 \qquad j<i. \tag{38b}$$

In this situation considering the $\Lambda_j\mathcal{R}^j\Lambda_k$ that occur in equation (20) $(k<j)$ and using equations (38*a*), (38*b*) we have

$$\Lambda_j\mathcal{R}^j\Lambda_k=\Lambda_j\mathcal{V}\Lambda_k+\Lambda_j\mathcal{V}Q_j(z-Q_j\mathcal{L}Q_j)^{-1}Q_j\mathcal{V}\Lambda_k$$

$$=\Lambda_j\mathcal{V}\Lambda_{j-1} \qquad k=j-1 \tag{39a}$$

$$=0 \qquad k<j-1. \tag{39b}$$

Hence in equation (20) for $\Lambda_i\mathcal{G}\Lambda_0$ only one path $\{i, i-1, i-2, \ldots, 1, 0\}$ contributes and we get

$$\Lambda_i\mathcal{G}(z)\Lambda_0=\Lambda_i\mathcal{G}^i(z)\Lambda_i\Lambda_i\mathcal{V}\Lambda_{i-1}\Lambda_{i-1}\mathcal{G}^{i-1}(z)\Lambda_{i-1}\ldots\Lambda_0\mathcal{G}^0(z)\Lambda_0 \qquad i\geqslant 1. \tag{40}$$

This expression is analogous to the result given by Cresser and Dalton (1980) (see equation (15)).

Considering the $\Lambda_i\mathcal{R}^{i-1}\Lambda_j$ $j<i$ that occur, via their Laplace transforms in the master equations (37) and using equations (38*a*), (38*b*) we find that

$$\Lambda_i\mathcal{R}^{i-1}\Lambda_j=\Lambda_i\mathcal{V}\Lambda_j+\Lambda_i\mathcal{V}Q_{i-1}(z-Q_{i-1}\mathcal{L}Q_{i-1})^{-1}Q_{i-1}\mathcal{V}\Lambda_j$$

$$=0 \qquad \text{for } j<i-1 \tag{41a}$$

$$=\Lambda_i\mathcal{R}^{i-1}\Lambda_{i-1} \qquad \text{for } j=i-1. \tag{41b}$$

Thus only $\Lambda_i\boldsymbol{R}^{i-1}(\tau)\Lambda_{i-1}$ is non-zero and the master equations (37) simplify to

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_i|\rho(t)\rangle\!\rangle=\Lambda_i\mathcal{H}\Lambda_i\Lambda_i|\rho(t)\rangle\!\rangle+\int_0^t \mathrm{d}\tau\,\Lambda_i\boldsymbol{R}^{i-1}(\tau)\Lambda_{i-1}\Lambda_{i-1}|\rho(t-\tau)\rangle\!\rangle \qquad i\geqslant 1. \tag{42}$$

We see that i is coupled to $i-1$, $i-1$ to $i-2$ and so on.

4.2. *Case B*

In this case the Λ_i are such that

$$\Lambda_i\mathcal{V}\Lambda_j=0 \qquad j<i-1 \quad \text{or} \quad j>i+1 \tag{43a}$$

$$Q_i\mathcal{V}\Lambda_j=0 \qquad j<i \tag{43b}$$

$$\Lambda_i \mathscr{V} Q_j = 0 \qquad j > i. \tag{43c}$$

Thus the conditions for case A are satisfied so that the equations (40), (42) will also apply here for case B.

In addition we have, using equation (21),

$$\Lambda_i \mathscr{R}^i \Lambda_i = \Lambda_i \mathscr{R}^{i+1} \Lambda_i + \Lambda_i \mathscr{R}^{i+1} \Lambda_{i+1} \Lambda_{i+1} \mathscr{G}^{i+1} \Lambda_{i+1} \Lambda_{i+1} \mathscr{R}^{i+1} \Lambda_i.$$

Then, using equations (43*b*), (43*c*) we find that

$$\Lambda_i \mathscr{R}^{i+1} \Lambda_i = \Lambda_i \mathscr{V} \Lambda_i + \Lambda_i \mathscr{V} Q_{i+1} (z - Q_{i+1} \mathscr{L} Q_{i+1})^{-1} Q_{i+1} \mathscr{V} \Lambda_i = \Lambda_i \mathscr{V} \Lambda_i. \tag{44a}$$

Also, using equation (43*c*) we obtain

$$\begin{aligned} \Lambda_i \mathscr{R}^{i+1} \Lambda_{i+1} &= \Lambda_i \mathscr{V} \Lambda_{i+1} + \Lambda_i \mathscr{V} Q_{i+1} (z - Q_{i+1} \mathscr{L} Q_{i+1})^{-1} Q_{i+1} \mathscr{V} \Lambda_{i+1} \\ &= \Lambda_i \mathscr{V} \Lambda_{i+1}. \end{aligned} \tag{44b}$$

As in equation (39*a*) we have

$$\Lambda_{i+1} \mathscr{R}^{i+1} \Lambda_i = \Lambda_{i+1} \mathscr{V} \Lambda_i. \tag{44c}$$

Thus we obtain the simplified result

$$\Lambda_i \mathscr{R}^i (z) \Lambda_i = \Lambda_i \mathscr{V} \Lambda_i + \Lambda_i \mathscr{V} \Lambda_{i+1} \Lambda_{i+1} \mathscr{G}^{i+1}(z) \Lambda_{i+1} \Lambda_{i+1} \mathscr{V} \Lambda_i. \tag{45}$$

This expression is very useful in calculating the $\Lambda_i \mathscr{R}^i \Lambda_i$ that occur in the $\Lambda_i \mathscr{G}^i \Lambda_i$. It also enables a continued fraction expression to be developed, analogous to a similar result given by Cresser and Dalton (1980, equation (16))

$$\begin{aligned} \Lambda_i \mathscr{R}^i \Lambda_i &= \Lambda_i \mathscr{V} \Lambda_i + \Lambda_i \mathscr{V} \Lambda_{i+1} (z - \mathscr{K} - \Lambda_{i+1} \mathscr{R}^{i+1} \Lambda_{i+1})^{-1} \Lambda_{i+1} \mathscr{V} \Lambda_i \\ &= \Lambda_i \mathscr{V} \Lambda_i + \Lambda_i \mathscr{V} \Lambda_{i+1} [z - \mathscr{K} - \Lambda_{i+1} \mathscr{V} \Lambda_{i+1} \\ &\quad - \Lambda_{i+1} \mathscr{V} \Lambda_{i+2} (z - \mathscr{K} - \Lambda_{i+2} \mathscr{R}^{i+2} \Lambda_{i+2})^{-1} \Lambda_{i+2} \mathscr{V} \Lambda_{i+1}]^{-1} \Lambda_{i+1} \mathscr{V} \Lambda_i \end{aligned} \tag{46}$$

etc.

It should be noted that the conditions given in equation (43) are not derivable from those in equation (38), since the Λ_i and Q_i are not in general Hermitian. Also the conditions in equations (38), (43) involving the Q_i are not derivable from those involving the Λ_i alone (equations (38*a*), (43*a*)). This is in contrast to the situation dealt with earlier (Cresser and Dalton 1980), in which the choice of the Λ_i as Hermitian projectors associated with successive manifolds of states leads to conditions (Cresser and Dalton 1980, equation (13)) analogous to those for case B.

In Liouville space the condition for case A may apply without those for case B, although in specific applications of the theory made so far the conditions for case B are satisfied.

5. Markoff approximation results

If the interaction Liouville operator $\mathscr{V}$ is zero, the $\Lambda_i |\rho\rangle\rangle$ change with time via $\exp(-i\mathscr{K}t/\hbar)\Lambda_i|\rho(0)\rangle\rangle$ as can easily be shown from equations (28), (37).

The Markoff approximation can apply in any specific equation (28), (37) when the various relaxation quantities $\Lambda_0 \boldsymbol{R}^0(\tau)\Lambda_0$, $\Lambda_i \boldsymbol{R}^{i-1}(\tau)\Lambda_j$ are only significant over a time scale (the correlation time τ_c) sufficiently short that the effects of the relaxation terms on the $\Lambda_0|\rho\rangle\rangle$, $\Lambda_j|\rho\rangle\rangle$ can be ignored over the time interval $(t, t-\tau)$.

If the Markoff approximation applies in the case of equation (28) we can then:

(i) replace $\Lambda_0|\rho(t-\tau)\rangle\rangle$ by $\exp(\mathrm{i}\mathscr{K}\tau/\hbar)\Lambda_0|\rho(t)\rangle\rangle$

(ii) replace $\int_0^t \mathrm{d}\tau$ by $\int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\varepsilon\tau}$ on the right hand side of the equation. ε is a suitably small quantity ($\varepsilon \geqslant 0$).

Using equation ($10a$), the master equation (28) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}(\Lambda_0|\rho(t)\rangle\rangle)=\frac{1}{\mathrm{i}\hbar}\mathscr{K}(\Lambda_0|\rho(t)\rangle\rangle)$$
$$+\left(\frac{1}{\mathrm{i}\hbar}\int_0^\infty \mathrm{d}\tau\ \Lambda_0 R^0(\tau)\Lambda_0 \exp[\mathrm{i}(\mathscr{K}+\mathrm{i}\hbar\varepsilon)\tau/\hbar]\right)(\Lambda_0|\rho(t)\rangle\rangle). \tag{47}$$

This is now a differential equation rather than an integro-differential equation.

Substituting for $R^0(\tau)$ from equation ($22a$), and doing the time integral in the last equation, we obtain the Markovian master equation (48)

$$\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_0|\rho\rangle\rangle=\frac{1}{\mathrm{i}\hbar}\mathscr{K}\Lambda_0|\rho\rangle\rangle+\Gamma^0\Lambda_0|\rho\rangle\rangle. \tag{48}$$

The Markovian relaxation operator is given by

$$\Gamma^0=\frac{1}{2\pi}\int \mathrm{d}\omega\ \Lambda_0\mathscr{R}^0(\hbar\omega)\Lambda_0\Lambda_0(\hbar\omega-\mathrm{i}\hbar\varepsilon-\mathscr{K})^{-1}\Lambda_0 \qquad \varepsilon>\operatorname{Im}\omega. \tag{49}$$

The Markoff approximation will be valid if $\Gamma\tau_c \ll 1$, where Γ is a typical matrix element of Γ^0.

Analogous equations can be obtained from equations (37), when the Markoff approximation is valid. As will be seen in paper II, it is possible for the Markoff approximation to apply for certain $\Lambda_i|\rho\rangle\rangle$ without necessarily applying for *all* $i=0, 1, 2, \ldots$.

Acknowledgments

I should like to thank Professor J Eberly and Dr P L Knight for helpful discussions and for kindly reading the manuscript. I should also like to acknowledge the hospitality of the Optics Section, Blackett Laboratory, Imperial College, London, during the final stages of preparing this paper.

Appendix 1. Liouville space

The notations and definitions for vectors and operators in Liouville space (L-space) used here follow those given by Cohen-Tannoudji (1975), along with some additional quantities used by Fiutak and van Kranendonk (1962). As this material is not widely available, we include it for reasons of completeness.

Each linear operator A in state space corresponds to a vector $|A\rangle\rangle$ in L-space such that

$$A+B \leftrightarrow |A\rangle\rangle+|B\rangle\rangle \tag{A1.1a}$$
$$cA \leftrightarrow c|A\rangle\rangle. \tag{A1.1b}$$

These definitions lead to the usual formal rules for sums of vectors in L-space, for example $|A\rangle\rangle + |B\rangle\rangle = |B\rangle\rangle + |A\rangle\rangle$.

Particular operators in state space are associated with L-space vectors defined as follows:

$$|i\rangle\langle j| \leftrightarrow |ij^{\dagger}\rangle\rangle \tag{A1.2a}$$

$$0 \leftrightarrow |0\rangle\rangle \tag{A1.2b}$$

$$1 \leftrightarrow |1\rangle\rangle. \tag{A1.2c}$$

Hence we have for orthonormal basis $|i\rangle$ in state space

$$|1\rangle\rangle = \sum_i |ii^{\dagger}\rangle\rangle \tag{A1.3a}$$

$$A = \sum_{ij} A_{ij}|i\rangle\langle j| \leftrightarrow |A\rangle\rangle = \sum_{ij} A_{ij}|ij^{\dagger}\rangle\rangle \tag{A1.3b}$$

so that the vectors $|ij^{\dagger}\rangle\rangle$ form a basis in L-space. As we shall see this basis is also orthonormal (see equation (A1.5*e*)).

The *scalar product* of two L-space vectors is defined via

$$\langle\langle B|A\rangle\rangle = \mathrm{Tr}(B^{\dagger}A) \tag{A1.4a}$$

$$= \sum_{ij} B^{*}_{ij}A_{ij} \qquad \text{in any orthonormal basis.} \tag{A1.4b}$$

The scalar product thus has the following properties

(i) $$\langle\langle A|A\rangle\rangle \geqslant 0 \tag{A1.5a}$$

(with equality only if $|A\rangle\rangle = |0\rangle\rangle$)

(ii) $$\langle\langle A|B\rangle\rangle = \langle\langle B|A\rangle\rangle^{*} \tag{A1.5b}$$

(iii) $$\mathrm{Tr}\, A = \langle\langle 1|A\rangle\rangle \tag{A1.5c}$$

(iv) $$\langle\langle ab^{\dagger}|cd^{\dagger}\rangle\rangle = \langle a|c\rangle\langle b|d\rangle^{*} \tag{A1.5d}$$

(v) $$\langle\langle ij^{\dagger}|kl^{\dagger}\rangle\rangle = \delta_{ik}\delta_{jl} \tag{A1.5e}$$

if $|i\rangle$ is an orthonormal basis in state space.

(vi) $$A_{ij} = \langle\langle ij^{\dagger}|A\rangle\rangle \tag{A1.5f}$$

if $|i\rangle$ is an orthonormal basis in state space.

Linear operators in L-space (super operators) can be defined in the situation where $A \to B(A)$ for all A via some linear relationship. In this case we may write

$$|B\rangle\rangle = F|A\rangle\rangle \tag{A1.6}$$

where F is a linear operator in L-space which expresses the particular linear relationship. As an example of a super operator consider the linear relationship

$$B = F_1 A F_2^{\dagger}. \tag{A1.7a}$$

We thus define

$$F = F_1 \times F_2^{\dagger} \tag{A1.7b}$$

$$|B\rangle\rangle = F|A\rangle\rangle \tag{A1.7c}$$

$$= |(F_1 A F_2^{\dagger})\rangle\rangle. \tag{A1.7d}$$

The *sum and product* of two super operators are defined in the usual way

$$(FG)|A\rangle\rangle = F(G|A\rangle\rangle) \tag{A1.8a}$$

$$(F+G)|A\rangle\rangle = F|A\rangle\rangle + G|A\rangle\rangle. \tag{A1.8b}$$

Super operators obey the usual rules of operator algebra, for example $(FG)H = F(GH) = FGH$.

The *Hermitian adjoint* $F^{\dagger}$ is defined to be such that

$$\langle\langle B|(F^{\dagger}|A\rangle\rangle) = \langle\langle A|(F|B\rangle\rangle)^*. \tag{A1.9}$$

All the usual rules for Hermitian adjoints follow, for example $(F^{\dagger})^{\dagger} = F$.

The *eigenvalue equation* for a super operator is of the usual form

$$F|\Lambda\rangle\rangle = \lambda|\Lambda\rangle\rangle. \tag{A1.10}$$

The usual results for eigenvalues and eigenvectors apply, for example if F is Hermitian then the eigenvalues are real.

The super operator $F = F_1 \times F_2^{\dagger}$ has a number of important *properties*

(i) $$(F_1 \times F_2^{\dagger})|ij^{\dagger}\rangle\rangle = |(F_1|i\rangle)(F_2|j\rangle)^{\dagger}\rangle\rangle \tag{A1.11a}$$

(ii) $$\langle\langle ab^{\dagger}|(F_1 \times F_2^{\dagger})|cd^{\dagger}\rangle\rangle = \langle a|F_1|c\rangle\langle b|F_2|d\rangle^* \tag{A1.11b}$$

(iii) $$(F_1 \times F_2^{\dagger})(G_1 \times G_2^{\dagger}) = (F_1G_1) \times (F_2G_2)^{\dagger} \tag{A1.11c}$$

(iv) $$c(F_1 \times F_2^{\dagger}) = (cF_1) \times F_2^{\dagger} = F_1 \times (c^*F_2)^{\dagger} \tag{A1.11d}$$

(v) $$(F_1 \times F_2^{\dagger})^{\dagger} = (F_1^{\dagger} \times F_2) \tag{A1.11e}$$

(vi) $$(F_1 + F_2) \times G^{\dagger} = F_1 \times G^{\dagger} + F_2 \times G^{\dagger} \tag{A1.11f}$$

$$F \times (G_1 + G_2)^{\dagger} = F \times G_1^{\dagger} + F \times G_2^{\dagger} \tag{A1.11g}$$

(vii) $$1 \times 1 = 1 \quad \text{(the unit super operator)} \tag{A1.11h}$$

$$\left.\begin{matrix} 1 \times 0 \\ 0 \times 1 \end{matrix}\right\} = 0 \quad \text{(the null super operator).} \tag{A1.11i}$$

The *Liouville super operator* $\mathscr{L}$ is defined in terms of the Hamiltonian operator in state space ($H = H^{\dagger}$)

$$\mathscr{L} = H \times 1 - 1 \times H. \tag{A1.12}$$

Thus

$$\mathscr{L}|A\rangle\rangle = |HA\rangle\rangle - |AH\rangle\rangle \tag{A1.13a}$$

$$= |[H, A]\rangle\rangle \tag{A1.13b}$$

so that $\mathscr{L}$ has the effect of taking the commutator of the operator with H.

The eigenvalues of the Liouville super operator are the transition energies (energy differences) and thus are related directly to the spectral transition line frequencies.

Because of this connection Liouville space is often also called *line space*. For with

$$H|i\rangle = E_i|i\rangle = \hbar\omega_i|i\rangle \tag{A1.14a}$$

we have

$$\mathscr{L}|ij^{\dagger}\rangle\rangle = \hbar\omega_{ij}|ij^{\dagger}\rangle\rangle. \tag{A1.14b}$$

The *Liouville equation* itself now becomes

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\rho\rangle\rangle = \mathscr{L}|\rho\rangle\rangle \tag{A1.15}$$

where $|\rho\rangle\rangle$ is the vector in L-space representing the density operator. The formal similarity of this form of the Liouville equation to the time-dependent Schrödinger equation is obvious.

An important property of $\mathscr{L}$ is that

$$\exp(\mathrm{i}\mathscr{L}t/\hbar)|A\rangle\rangle = |\exp(\mathrm{i}Ht/\hbar)A\exp(-\mathrm{i}Ht/\hbar)\rangle\rangle. \tag{A1.16}$$

This enables us to write down the solution of the Liouville equation for the case where H is independent of t

$$|\rho(t)\rangle\rangle = \exp(-\mathrm{i}\mathscr{L}t/\hbar)|\rho(0)\rangle\rangle \tag{A1.17a}$$

$$= |\exp(-\mathrm{i}Ht/\hbar)\rho(0)\exp(\mathrm{i}Ht/\hbar)\rangle\rangle. \tag{A1.17b}$$

Since H is Hermitian it is trivial to show also that $\mathscr{L}$ is Hermitian.

Another important type of super operator is the form $|A\rangle\rangle\langle\langle B|$ which is defined via

$$(|A\rangle\rangle\langle\langle B|)|C\rangle\rangle \equiv |A\rangle\rangle\langle\langle B|C\rangle\rangle. \tag{A1.18}$$

From the equations (A1.3*b*) and (A1.5*f*) for an orthonormal basis $|i\rangle$ we can easily obtain the completeness relationship

$$1 = \sum_{ij}|ij^{\dagger}\rangle\rangle\langle\langle ij^{\dagger}|. \tag{A1.19}$$

State space is often the direct product of two subspaces R and S. If A_{R} and A_{S} are typical operators in R, S respectively then the product $A_{\mathrm{R}}A_{\mathrm{S}} = A_{\mathrm{S}}A_{\mathrm{R}}$ corresponds to the product of two vectors $|A_{\mathrm{R}}\rangle\rangle$, $|A_{\mathrm{S}}\rangle\rangle$ in separate L-spaces.

$$A_{\mathrm{R}}A_{\mathrm{S}} \leftrightarrow |A_{\mathrm{R}}\rangle\rangle|A_{\mathrm{S}}\rangle\rangle \equiv |A_{\mathrm{S}}\rangle\rangle|A_{\mathrm{R}}\rangle\rangle. \tag{A1.20}$$

Thus we can consider the direct product of two Liouville spaces.

If $|ij^{\dagger}\rangle\rangle$ is a basis in the S part of L-space, $|\alpha\beta^{\dagger}\rangle\rangle$ in the R part of L-space R, then $|ij^{\dagger};\alpha\beta^{\dagger}\rangle\rangle \equiv |ij^{\dagger}\rangle\rangle|\alpha\beta^{\dagger}\rangle\rangle$ will be a basis in the overall L-space.

Similarly we may have super operators of the form $F_{\mathrm{R}}F_{\mathrm{S}}$ (strictly $F_{\mathrm{R}}\otimes F_{\mathrm{S}}$) (or sums of products etc) such that $F_{\mathrm{R}}F_{\mathrm{S}}|A_{\mathrm{R}}\rangle\rangle|A_{\mathrm{S}}\rangle\rangle \equiv (F_{\mathrm{R}}|A_{\mathrm{R}}\rangle\rangle)(F_{\mathrm{S}}|A_{\mathrm{S}}\rangle\rangle)$.

Appendix 2. Derivation of resolvent operator theory results

A2.1. Expressions for $\Lambda_0\mathscr{G}\Lambda_0$ and $Q_0\mathscr{G}\Lambda_0$

$$(z-\mathscr{L})\mathscr{G}(z) = 1. \tag{A2.1}$$

Substituting $1=\Lambda_0+Q_0$ between $z-\mathscr{L}$ and $\mathscr{G}$ in (A2.1), multiplying from the right by Λ_0 and then using (5a), (7f) for $i=0$, we obtain

$$(z-\mathscr{L})\Lambda_0\Lambda_0\mathscr{G}(z)\Lambda_0+(z-\mathscr{L})Q_0Q_0\mathscr{G}(z)\Lambda_0=\Lambda_0. \tag{A2.2}$$

Multiplying (A2.2) from the left by Λ_0 and using (5a), (7c), (10a) for $i=0$, we obtain

$$\Lambda_0(z-\mathscr{L})\Lambda_0\Lambda_0\mathscr{G}(z)\Lambda_0-\Lambda_0\mathscr{V}Q_0Q_0\mathscr{G}(z)\Lambda_0=\Lambda_0. \tag{A2.3}$$

Multiplying (A2.2) from the left by Q_0, and using (7c), (7f) and (10a) for $i=0$, we obtain

$$-Q_0\mathscr{V}\Lambda_0\Lambda_0\mathscr{G}(z)\Lambda_0+Q_0(z-Q_0\mathscr{L}Q_0)Q_0Q_0\mathscr{G}(z)\Lambda_0=0. \tag{A2.4}$$

Now

$$(z-Q_0\mathscr{L}Q_0)^{-1}(z-Q_0\mathscr{L}Q_0)=1. \tag{A2.5}$$

Multiplying (A2.5) from the left and right by Q_0 and using (7f) with $i=0$, we obtain

$$Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0Q_0(z-Q_0\mathscr{L}Q_0)Q_0=Q_0. \tag{A2.6}$$

Hence we obtain from (A2.4), using (7f) with $i=0$

$$Q_0\mathscr{G}(z)\Lambda_0=Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0Q_0\mathscr{V}\Lambda_0\Lambda_0\mathscr{G}(z)\Lambda_0. \tag{A2.7}$$

Substituting this result into (A2.3), using (5a), (7f) with $i=0$, we have

$$\Lambda_0[z-\mathscr{H}-\Lambda_0\mathscr{V}\Lambda_0-\Lambda_0\mathscr{V}Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0\mathscr{V}\Lambda_0]\Lambda_0\Lambda_0\mathscr{G}(z)\Lambda_0=1. \tag{A2.8}$$

The line shift operator $\mathscr{R}^0(z)$ is introduced via

$$\mathscr{R}^0(z)=\mathscr{V}+\mathscr{V}Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0\mathscr{V}. \tag{A2.9}$$

Substituting for $\mathscr{R}^0(z)$ in (2.8), we get

$$\Lambda_0(z-\mathscr{H}-\Lambda_0\mathscr{R}^0(z)\Lambda_0)\Lambda_0\mathscr{G}(z)\Lambda_0=1. \tag{A2.10}$$

Similarly to the derivation of (A2.6) we then find

$$\Lambda_0(z-\mathscr{H}-\Lambda_0\mathscr{R}^0\Lambda_0)^{-1}\Lambda_0\Lambda_0(z-\mathscr{H}-\Lambda_0\mathscr{R}^0\Lambda_0)\Lambda_0=\Lambda_0. \tag{A2.11}$$

Hence from (A2.10) and using (5a) with $i=0$, we obtain

$$\Lambda_0\mathscr{G}(z)\Lambda_0=\Lambda_0\mathscr{G}^0(z)\Lambda_0 \tag{A2.12}$$

where we have defined the reduced resolvent operator $\Lambda_0\mathscr{G}^0(z)\Lambda_0$ as in (A2.13)

$$\Lambda_0\mathscr{G}^0(z)\Lambda_0=\Lambda_0(z-\mathscr{H}-\Lambda_0\mathscr{R}^0(z)\Lambda_0)^{-1}\Lambda_0. \tag{A2.13}$$

Also from (A2.9), and using (7f) with $i=0$, we have

$$\begin{aligned}Q_0\mathscr{R}^0(z)\Lambda_0&=[1+Q_0\mathscr{V}Q_0(z-Q_0\mathscr{L}Q_0)^{-1}]Q_0\mathscr{V}\Lambda_0\\&=[(z-Q_0\mathscr{L}Q_0)(z-Q_0\mathscr{L}Q_0)^{-1}+Q_0\mathscr{V}Q_0(z-Q_0\mathscr{L}Q_0)^{-1}]Q_0\mathscr{V}\Lambda_0\\&=(z-Q_0\mathscr{H}Q_0)(z-Q_0\mathscr{L}Q_0)^{-1}Q_0\mathscr{V}Q_0\\&=Q_0(z-Q_0\mathscr{H}Q_0)Q_0Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0Q_0\mathscr{V}Q_0.\end{aligned} \tag{A2.14}$$

If we use an expression analogous to (A2.6) with $\mathscr{H}$ replacing $\mathscr{L}$, we then get from (A2.14)

$$Q_0(z-Q_0\mathscr{L}Q_0)^{-1}Q_0Q_0\mathscr{V}Q_0=Q_0(z-Q_0\mathscr{H}Q_0)^{-1}Q_0Q_0\mathscr{R}^0(z)\Lambda_0. \tag{A2.15}$$

Substituting (A2.15), (A2.12) into (A2.7) gives

$$Q_0\mathscr{G}(z)\Lambda_0 = Q_0(z-Q_0\mathscr{H}Q_0)^{-1}Q_0Q_0\mathscr{R}^0(z)\Lambda_0\Lambda_0\mathscr{G}^0(z)\Lambda_0. \tag{A2.16}$$

A2.2. Derivation of the identity $\mathscr{R}^{i-1} = \mathscr{R}^i + \mathscr{R}^i\Lambda_i\mathscr{G}^i\Lambda_i\mathscr{R}^i$

$$(z-Q_{i-1}\mathscr{L}Q_{i-1})(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1} = 1. \tag{A2.17}$$

Multiplying (A2.17) from the left and right by Q_{i-1} and using (7*f*) for the case $i-1$, we obtain

$$(z-Q_{i-1}\mathscr{L}Q_{i-1})Q_{i-1}(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} = Q_{i-1}. \tag{A2.18}$$

If we use (7*a*) to replace Q_{i-1} by $Q_i+\Lambda_i$ in the left and middle factor of (A2.18) we obtain

$$[z-(Q_i+\Lambda_i)\mathscr{L}(Q_i+\Lambda_i)](Q_i+\Lambda_i)(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} = Q_{i-1}. \tag{A2.19}$$

Multiplying (A2.19) from the left by Q_i, using (7*g*) for the case $j=i-1$, (7*c*), and (7*f*), we get

$$Q_i(z-Q_i\mathscr{L}Q_i)Q_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} - Q_i\mathscr{L}\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} = Q_i. \tag{A2.20}$$

Multiplying (A2.19) from the left by Λ_i, using (7*e*) for the case $j=i-1$, (7*c*), (7*f*) and (5*a*), we get

$$\Lambda_i(z-\Lambda_i\mathscr{L}\Lambda_i)\Lambda_i\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} - \Lambda_i\mathscr{L}Q_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} = \Lambda_i. \tag{A2.21}$$

From $(z-Q_i\mathscr{L}Q_i)^{-1}(z-Q_i\mathscr{L}Q_i)=1$ we obtain on multiplying from the right by Q_i and using (7*f*),

$$(z-Q_i\mathscr{L}Q_i)^{-1}Q_i(z-Q_i\mathscr{L}Q_i)Q_i = Q_i. \tag{A2.22}$$

Multiplying (A2.20) from the left by $(z-Q_i\mathscr{L}Q_i)^{-1}$ and using (A2.22) and using (5*a*), we obtain

$$\begin{aligned} &Q_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} \\ &\quad = (z-Q_i\mathscr{L}Q_i)^{-1}Q_i + (z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{L}\Lambda_i\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}. \end{aligned} \tag{A2.23}$$

Substituting for $Q_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}$ from (A2.23) into (A2.21) and using (7*f*), we find that

$$\begin{aligned} &\Lambda_i(z-\Lambda_i\mathscr{L}\Lambda_i)\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} - \Lambda_i\mathscr{L}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i \\ &\qquad - \Lambda_i\mathscr{L}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{L}\Lambda_i\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1} \\ &\quad = \Lambda_i. \end{aligned} \tag{A2.24}$$

Hence, using (7*c*) and (10*a*)

$$\begin{aligned} &\Lambda_i + \Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i \\ &\quad = \Lambda_i[z-\Lambda_i\mathscr{H}\Lambda_i - \Lambda_i\mathscr{V}\Lambda_i - \Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}\Lambda_i]\Lambda_i \\ &\qquad \times \Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}. \end{aligned} \tag{A2.25}$$

We then introduce the line shift operator $\mathscr{R}^i(z)$ via (A2.26)

$$\mathscr{R}^i(z)=\mathscr{V}+\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}. \tag{A2.26}$$

Hence

$$\Lambda_i(z-\mathscr{K}-\Lambda_i\mathscr{R}^i(z)\Lambda_i)\Lambda_i\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}$$
$$=\Lambda_i+\Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i. \tag{A2.27}$$

Similarly to (A2.11) we can derive the result

$$\Lambda_i(z-\mathscr{K}-\Lambda_i\mathscr{R}^i\Lambda_i)^{-1}\Lambda_i\Lambda_i(z-\mathscr{K}-\Lambda_i\mathscr{R}^i\Lambda_i)=\Lambda_i. \tag{A2.28}$$

The reduced resolvent operator is introduced via

$$\Lambda_i\mathscr{G}^i(z)\Lambda_i=\Lambda_i(z-\mathscr{K}-\Lambda_i\mathscr{R}^i(z)\Lambda_i)^{-1}\Lambda_i. \tag{A2.29}$$

Using (A2.28), (A2.29) in (A2.27) we obtain

$$\Lambda_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}=\Lambda_i\mathscr{G}^i\Lambda_i[\Lambda_i+\Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i]. \tag{A2.30}$$

Substituting (A2.30) into (A2.23), using (7c) and (10a) and then multiplying from the left by Q_i, we find that

$$Q_i(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}$$
$$=Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i$$
$$+Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}\Lambda_i\Lambda_i\mathscr{G}^i\Lambda_i[\Lambda_i+\Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i]. \tag{A2.31}$$

Adding (A2.31) and (A2.30), replacing Q_{i-1} by Λ_i+Q_i from (7a), and using (5a), we obtain

$$Q_{i-1}(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}$$
$$=Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i+[\Lambda_i+Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}\Lambda_i]\Lambda_i\mathscr{G}^i\Lambda_i$$
$$\times(\Lambda_i+\Lambda_i\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i). \tag{A2.32}$$

Multiplying (A2.32) from the left and right by $\mathscr{V}$, then adding $\mathscr{V}$ to each side, and using (5a), we get

$$\mathscr{V}+\mathscr{V}Q_{i-1}(z-Q_{i-1}\mathscr{L}Q_{i-1})^{-1}Q_{i-1}\mathscr{V}$$
$$=\mathscr{V}+\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}$$
$$+(\mathscr{V}+\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V})\Lambda_i\mathscr{G}^i\Lambda_i(\mathscr{V}+\mathscr{V}Q_i(z-Q_i\mathscr{L}Q_i)^{-1}Q_i\mathscr{V}).$$

This result is the same as

$$\mathscr{R}^{i-1}(z)=\mathscr{R}^i(z)+\mathscr{R}^i(z)\Lambda_i\mathscr{G}^i(z)\Lambda_i\mathscr{R}^i(z). \tag{A2.33}$$

A2.3. Derivation of expression for $\Lambda_i\mathscr{G}\Lambda_0 (i\geqslant 1)$

Using induction it is easy to see that (A2.33) yields the identity

$$\mathscr{R}^0(z)=\mathscr{R}^i(z)\prod_{j=1}^{i}(1+\Lambda_j\mathscr{G}^j(z)\Lambda_j\mathscr{R}^j(z)) \tag{A2.34}$$

where the product is ordered with the $j=1$ factor on the right.

Substituting (A2.34) into (A2.16) gives

$$Q_0\mathcal{G}(z)\Lambda_0 = Q_0(z - Q_0\mathcal{H}Q_0)^{-1}Q_0Q_0\mathcal{R}^i(z) \times \prod_{j=1}^{i}(1+\Lambda_j\mathcal{G}^j(z)\Lambda_j\mathcal{R}^j(z))\Lambda_0\Lambda_0\mathcal{G}^0(z)\Lambda_0. \quad \text{(A2.35)}$$

From $(7b)$ with $j=0$ we can write

$$Q_0 = \Lambda_1 + \Lambda_2 + \ldots. + \Lambda_i + Q_i. \quad \text{(A2.36)}$$

Multiplying (A2.35) from the left by Λ_i, using $(7e)$ with $j=0$, we obtain

$$\Lambda_i\mathcal{G}(z)\Lambda_0 = \Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}Q_0Q_0\mathcal{R}^i\prod_{j=1}^{i}(1+\Lambda_j\mathcal{G}^j\Lambda_j\mathcal{R}^j)\Lambda_0\Lambda_0\mathcal{G}^0\Lambda_0. \quad \text{(A2.37)}$$

Now

$$(z - Q_0\mathcal{H}Q_0)^{-1}(z - Q_0\mathcal{H}Q_0) = 1. \quad \text{(A2.38)}$$

Multiplying (A2.38) from the left by Λ_i we get

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}(z - Q_0\mathcal{H}Q_0) = \Lambda_i. \quad \text{(A2.39)}$$

Multiplying (A2.39) from the right by $\Lambda_j (j = 1, 2, \ldots, i-1)$, using $(5b)$, using $Q_0\Lambda_j = \Lambda_j$ (from $(7e)$) twice, using $\mathcal{H}\Lambda_j = \Lambda_j\mathcal{H}$ (from $(10a)$) and $\Lambda_j^2 = \Lambda_j$ (from $(5a)$), we get

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}\Lambda_j(z - \Lambda_j\mathcal{H}\Lambda_j) = 0 \qquad j = 1, 2, \ldots, i-1. \quad \text{(A2.40)}$$

Multiplying (A2.40) from the right by $(z - \Lambda_j\mathcal{H}\Lambda_j)^{-1}$ gives

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}\Lambda_j = 0 \qquad j = 1, 2, \ldots, i-1. \quad \text{(A2.41)}$$

Multiplying (A2.39) on the right by Λ_i, using $(5a)$ twice, using $Q_0\Lambda_i = \Lambda_i$ (from $(7e)$) twice, and also $(10a)$, we obtain

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}\Lambda_i(z - \Lambda_i\mathcal{H}\Lambda_i) = \Lambda_i. \quad \text{(A2.42)}$$

Multiplying (A2.42) from the right by $(z - \Lambda_i\mathcal{H}\Lambda_i)^{-1}$ and then by Λ_i, and using $(5a)$, we find that

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}\Lambda_i = \Lambda_i(z - \Lambda_i\mathcal{H}\Lambda_i)^{-1}\Lambda_i. \quad \text{(A2.43)}$$

Multiplying (A2.39) on the right by Q_i, using $(7c)$, using $Q_0Q_i = Q_i$ (from $(7h)$) twice, using also $(10b)$ and $(7f)$, we get

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}Q_i(z - Q_i\mathcal{H}Q_i) = 0. \quad \text{(A2.44)}$$

Multiplying (A2.44) from the right by $(z - Q_i\mathcal{H}Q_i)^{-1}$ then gives

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}Q_i = 0. \quad \text{(A2.45)}$$

Adding the equations (A2.45), (A2.43) and the equations (A2.41) for $j = 1, 2, \ldots, i-1$, and on using (A2.36), we then get

$$\Lambda_i(z - Q_0\mathcal{H}Q_0)^{-1}Q_0 = \Lambda_i(z - \Lambda_i\mathcal{H}\Lambda_i)^{-1}\Lambda_i. \quad \text{(A2.46)}$$

Substituting (A2.46) into (A2.37), using $\Lambda_iQ_0 = \Lambda_i$ (from $(7e)$) and $(5a)$, we obtain

$$\Lambda_i\mathcal{G}(z)\Lambda_0 = \Lambda_i(z - \Lambda_i\mathcal{H}\Lambda_i)^{-1}\Lambda_i\Lambda_i\mathcal{R}^i(z)\prod_{j=1}^{i}(1+\Lambda_j\mathcal{G}^j(z)\Lambda_j\mathcal{R}^j(z))\Lambda_0\Lambda_0\mathcal{G}^0(z)\Lambda_0. \quad \text{(A2.47)}$$

This expression is analogous to (5*b*) in Cresser and Dalton (1980). The derivation of the final equation, which is analogous to (12) in the last reference, follows the procedures outlined therein, with appropriate changes of notation.

Thus we have

$$\Lambda_i \mathscr{G}(z)\Lambda_0 = \sum_{\substack{\text{paths} \\ \{i, j, \ldots, 0\}}} \Lambda_i \mathscr{G}^i(z)\Lambda_i\Lambda_i\mathscr{R}^i(z)\Lambda_j\Lambda_j\mathscr{G}^j(z)\Lambda_j\Lambda_j\mathscr{R}^j(z)\ldots\Lambda_0\mathscr{G}^0(z)\Lambda_0. \tag{A2.48}$$

References

Agarwal G S 1973 *Prog. Opt.* **9** 3–76

—— 1974 *Springer Tracts in Modern Physics* vol 70 (Berlin: Springer)

Argyres P N and Kelley P L 1964 *Phys. Rev.* **134** A98–111

Cohen-Tannoudji C 1975 *Cours de Physique Atomique et Moleculaire* College de France

—— 1977 *Frontiers in Laser Spectroscopy*: *Les Houches* session 27, ed R Balian, S Haroche and S Liberman (Amsterdam: North-Holland)

Cresser J D and Dalton B J 1980 *J. Phys. A: Math. Gen.* **13** 795–801

Dalton B J 1982 *J. Phys. B: At. Mol. Phys.* **15** 553–60

Fiutak J and Van Kranendonk J 1962 *Can. J. Phys.* **40** 1085–100

Goldberger M L and Watson K M 1964 *Collision Theory* (New York: Wiley) p 433

Haake F 1973 *Springer Tracts in Modern Physics* vol 66 (Berlin: Springer)

Morse P M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw-Hill) pp 484, 1579

Mower L 1966 *Phys. Rev.* **142** 799–816

—— 1968 *Phys. Rev.* **165** 145–57

Nakajima S 1958 *Prog. Theor. Phys.* **20** 948–59

Zwanzig R 1961 *Lectures in Theoretical Physics* vol 3, ed W E Britten (New York: Wiley)

—— 1964 *Physica* **30** 1109–23