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Liouville space theory of sequential quantum processes: II. Application to a system with an internal reservoir

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Abstract. A system consisting of discrete states and continuum states (which form a so-called internal reservoir) is treated, illustrating the theory of sequential quantum processes in Liouville space developed in the preceding paper. The populations and coherences associated with the discrete states satisfy Markovian master equations when the interaction matrix elements between discrete and continuum states are significant over a broad band of continuum states. The population of a single discrete state decays exponentially with time, whilst the population of two coupled discrete states (one only coupled to the continuum states) may exhibit Rabi oscillations. For the latter case of two coupled discrete levels, the population of particular continuum states approaches a two-peak form for long times (Autler–Townes splitting).

1. Introduction

In the preceding paper (Dalton 1982) (to be referred to as I) the general theory of sequential quantum processes in Liouville space was developed. In this paper we illustrate the theory by applying it to a system with an internal reservoir.

We consider a system with two types of states, which are eigenstates of a certain zeroth-order Hamiltonian. The states $|i\rangle$ (with energy $\hbar\omega_i$) are discrete states, and constitute what we shall refer to as the small system, S. The other states $|\alpha\rangle$ (with energy $\hbar\omega_\alpha$) are continuum states, and can be considered as constituting a large quantum system or reservoir, R. Both types of states are of course states of the same overall quantum system, as distinct from the case discussed in § 1 of I, where S and R were separate quantum systems. In that case R, with its states $|A\rangle$ being associated with different coordinates from those for the states $|i\rangle$ of S, can be referred to as an *external reservoir*. In the present case the states constituting R can be referred to as an *internal reservoir*.

Such a situation occurs in the case of atomic autoionisation. The states $|i\rangle$ are the discrete atomic states, the states $|\alpha\rangle$ are the continuum atomic states, both associated with a zeroth-order atomic Hamiltonian, which may, for example, not include certain inter-electronic interactions.

The system is subject to an interaction V, which causes transitions amongst the states $|i\rangle$, $|\alpha\rangle$. This interaction could be due to an external field or could represent an internal interaction, for example an inter-electronic interaction that causes autoionisation.

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Suppose that at $t=0$ the only non-zero elements of the density operator ρ are between various system states $|i\rangle$, $|j\rangle$. The problem is to calculate:

(i) the populations ρ_{ii} and coherences $\rho_{ij}(i \neq j)$ associated with system states as a function of time,

(ii) the populations $\rho_{\alpha\alpha}$ of continuum states $|\alpha\rangle$.

The basic quantities required are introduced in § 2. In § 3 we determine the system populations and coherences, specialising the results to two cases, (i) a single discrete state coupled to the continuum, (ii) two coupled discrete states, one also coupled to the continuum. The population of the reservoir states is dealt with in § 4, for the special case just referred to.

2. Basic quantities for the system

The Hamiltonian is

$$H = H_S + H_R + V_{SR} \tag{1a}$$

$$= K + V_{SR} \tag{1b}$$

where H_S, H_R, V_{SR} are the system Hamiltonian, the reservoir Hamiltonian and the system–reservoir interaction respectively. These are defined via

$$H_S = H_{S0} + V_S \tag{2a}$$

$$H_{S0} = \sum_i \hbar\omega_i |i\rangle\langle i| \tag{2b}$$

$$V_S = \sum_{ij} \hbar v_{ij} |i\rangle\langle j| \tag{2c}$$

$$H_R = H_{R0} + V_R \tag{2d}$$

$$H_{R0} = \sum_\alpha \hbar\omega_\alpha |\alpha\rangle\langle\alpha| \tag{2e}$$

$$V_R = \sum_\alpha \hbar v_{\alpha\beta} |\alpha\rangle\langle\beta| \tag{2f}$$

$$V_{SR} = \sum_{i\alpha} \hbar(v_{\alpha i}|\alpha\rangle\langle i| + v_{i\alpha}|i\rangle\langle\alpha|). \tag{2g}$$

The quantities $\hbar v_{ij}, \hbar v_{\alpha\beta}, \hbar v_{\alpha i}, \hbar v_{i\alpha}$ are matrix elements of V between the relevant states. Only that part of V that causes system–reservoir transitions has been included in V_{SR}, the remaining parts of V are included in H_S or H_R. In terms of the general theory (see I) the unperturbed Hamiltonian K is the sum of the system and reservoir Hamiltonians.

We introduce Hermitian projectors $\mathscr{P}$, $\mathscr{Q}$ in state vector space via

$$\mathscr{P} = \sum_i |i\rangle\langle i| \tag{3a}$$

$$\mathscr{Q} = \sum_\alpha |\alpha\rangle\langle\alpha|. \tag{3b}$$

These satisfy the conditions

$$\mathcal{P}+\mathcal{Q}=1 \tag{4a}$$

$$\mathcal{P}^2=\mathcal{P} \tag{4b}$$

$$\mathcal{Q}^2=\mathcal{Q} \tag{4c}$$

$$\mathcal{P}\mathcal{Q}=\mathcal{Q}\mathcal{P}=0 \tag{4d}$$

$$\mathcal{P}H_{\mathrm{S}}=H_{\mathrm{S}}\mathcal{P}=H_{\mathrm{S}} \tag{4e}$$

$$\mathcal{P}H_{\mathrm{R}}=H_{\mathrm{R}}\mathcal{P}=0 \tag{4f}$$

$$\mathcal{Q}H_{\mathrm{S}}=H_{\mathrm{S}}\mathcal{Q}=0 \tag{4g}$$

$$\mathcal{Q}H_{\mathrm{R}}=H_{\mathrm{R}}\mathcal{Q}=H_{\mathrm{R}} \tag{4h}$$

$$\mathcal{P}V_{\mathrm{SR}}\mathcal{P}=\mathcal{Q}V_{\mathrm{SR}}\mathcal{Q}=0 \tag{4i}$$

$$\mathcal{P}V_{\mathrm{SR}}\mathcal{Q}=\sum_{i\alpha}\hbar v_{i\alpha}|i\rangle\langle\alpha| \tag{4j}$$

$$\mathcal{Q}V_{\mathrm{SR}}\mathcal{P}=\sum_{i\alpha}\hbar v_{\alpha i}|\alpha\rangle\langle i|. \tag{4k}$$

The Hermitian projectors Λ_0, Λ_1, Λ_2 are defined in Liouville space via

$$\Lambda_0=\mathcal{P}\times\mathcal{P}^{\dagger} \tag{5a}$$

$$\Lambda_1=\mathcal{P}\times\mathcal{Q}^{\dagger}+\mathcal{Q}\times\mathcal{P}^{\dagger} \tag{5b}$$

$$\Lambda_2=\mathcal{Q}\times\mathcal{Q}^{\dagger}. \tag{5c}$$

It is then found that

$$\Lambda_0=\sum_{ij}|ij^{\dagger}\rangle\!\rangle\langle\!\langle ij^{\dagger}| \tag{6a}$$

$$\Lambda_1=\sum_{i\alpha}(|i\alpha^{\dagger}\rangle\!\rangle\langle\!\langle i\alpha^{\dagger}|+|\alpha i^{\dagger}\rangle\!\rangle\langle\!\langle \alpha i^{\dagger}|) \tag{6b}$$

$$\Lambda_2=\sum_{\alpha\beta}|\alpha\beta^{\dagger}\rangle\!\rangle\langle\!\langle \alpha\beta^{\dagger}| \tag{6c}$$

$$1=\Lambda_0+\Lambda_1+\Lambda_2 \tag{6d}$$

$$Q_0=\Lambda_1+\Lambda_2 \tag{6e}$$

$$Q_1=\Lambda_2 \tag{6f}$$

$$Q_2=0. \tag{6g}$$

The conditions given in equations (5) and (7) of I are also satisfied. In this case Λ_0 spans the subspace with basis vectors $|ij^{\dagger}\rangle\!\rangle$, Λ_1 spans the subspace with basis vectors $|i\alpha^{\dagger}\rangle\!\rangle$, $|\alpha i^{\dagger}\rangle\!\rangle$ and Λ_2 spans the subspace with basis vectors $|\alpha\beta^{\dagger}\rangle\!\rangle$.

Initially the system is in a mixed system state given by

$$|\rho(0)\rangle\!\rangle=\sum_{ij}\rho_{ij}(0)|ij^{\dagger}\rangle\!\rangle. \tag{7}$$

The conditions given in equation (8) of I are thus satisfied.

The unperturbed Liouville operator is given as in equation (9*b*) of I, with $K = H_S + H_R$, and can be written as $\mathscr{K} = \mathscr{K}_S + \mathscr{K}_R$ in an obvious notation. The interaction Liouville operator $\mathscr{V}$ is given as in equation (9*c*) of I, with $V = V_{SR}$.

It is then easily shown that the conditions given in equations (10) and (43) of I are satisfied. We find that

$$\Lambda_0\mathscr{V}\Lambda_0 = \Lambda_1\mathscr{V}\Lambda_1 = \Lambda_2\mathscr{V}\Lambda_2 = 0 \tag{8a}$$

$$\Lambda_0\mathscr{V}\Lambda_2 = \Lambda_2\mathscr{V}\Lambda_0 = 0 \tag{8b}$$

$$\Lambda_2\mathscr{K}_S = \mathscr{K}_S\Lambda_2 = 0 \tag{8c}$$

$$\Lambda_0\mathscr{K}_R = \mathscr{K}_R\Lambda_0 = 0. \tag{8d}$$

The only non-zero quantities of the form $\Lambda_i\mathscr{V}\Lambda_j$ are $\Lambda_0\mathscr{V}\Lambda_1$, $\Lambda_1\mathscr{V}\Lambda_2$, $\Lambda_1\mathscr{V}\Lambda_0$, $\Lambda_2\mathscr{V}\Lambda_1$. Their non-zero matrix elements in Liouville space can be calculated using equations (9*c*), (A1.9), (A1.11) of I and equation (2*g*) and are given by

$$\langle\langle ij^\dagger|\Lambda_0\mathscr{V}\Lambda_1|i\alpha^\dagger\rangle\rangle = -\hbar v^*_{j\alpha} \tag{9a}$$

$$\langle\langle ji^\dagger|\Lambda_0\mathscr{V}\Lambda_1|\alpha i^\dagger\rangle\rangle = \hbar v_{j\alpha} \tag{9b}$$

$$\langle\langle i\alpha^\dagger|\Lambda_1\mathscr{V}\Lambda_0|ij^\dagger\rangle\rangle = -\hbar v_{j\alpha} \tag{9c}$$

$$\langle\langle \alpha i^\dagger|\Lambda_1\mathscr{V}\Lambda_0|ji^\dagger\rangle\rangle = \hbar v^*_{j\alpha} \tag{9d}$$

$$\langle\langle \alpha i^\dagger|\Lambda_1\mathscr{V}\Lambda_2|\alpha\beta^\dagger\rangle\rangle = -\hbar v^*_{i\beta} \tag{9e}$$

$$\langle\langle i\alpha^\dagger|\Lambda_1\mathscr{V}\Lambda_2|\beta\alpha^\dagger\rangle\rangle = \hbar v_{i\beta} \tag{9f}$$

$$\langle\langle \alpha\beta^\dagger|\Lambda_2\mathscr{V}\Lambda_1|\alpha i^\dagger\rangle\rangle = -\hbar v_{i\beta} \tag{9g}$$

$$\langle\langle \beta\alpha^\dagger|\Lambda_2\mathscr{V}\Lambda_1|i\alpha^\dagger\rangle\rangle = \hbar v^*_{i\beta}. \tag{9h}$$

3. System populations and coherences

3.1. General case

The system populations and coherences can be obtained from the master equation (28) of I. To see whether the Markoff approximation applies we need to consider matrix elements $\langle\langle ij^\dagger|\Lambda_0 \boldsymbol{R}^0(\tau)\Lambda_0|lm^\dagger\rangle\rangle$ of the relaxation operator, which can be obtained as inverse Laplace transforms of the matrix elements $\langle\langle ij^\dagger|\Lambda_0\mathscr{R}^0(\hbar\omega)\Lambda_0|lm^\dagger\rangle\rangle$, using equation (22*a*) of I.

We make the weak-coupling approximation of replacing $\mathscr{L}$ by $\mathscr{K}$ in the expression (18) (see I) for $\mathscr{R}^0$. Using equations (6*e*), (8*a*), (8*b*), (8*c*) and equations (10*a*), (5*b*), (5*a*) of I we find that

$$\Lambda_0\mathscr{R}^0(z)\Lambda_0 \doteqdot \Lambda_0\mathscr{V}\Lambda_1\Lambda_1(z - \Lambda_1\mathscr{K}\Lambda_1 - \Lambda_2\mathscr{K}_R\Lambda_2)^{-1}\Lambda_1\Lambda_1\mathscr{V}\Lambda_0. \tag{10}$$

Similarly to the derivation of equation (A2.11) in I we can show that

$$\Lambda_1(z - \Lambda_1\mathscr{K}\Lambda_1 - \Lambda_2\mathscr{K}_R\Lambda_2)^{-1}\Lambda_1\Lambda_1(z - \Lambda_1\mathscr{K}\Lambda_1)\Lambda_1 = \Lambda_1. \tag{11}$$

The required matrix elements of $\Lambda_1(z - \Lambda_1\mathscr{K}\Lambda_1 - \Lambda_2\mathscr{K}_R\Lambda_2)^{-1}\Lambda_1$ can be obtained as the inverse of the matrix for $\Lambda_1(z - \Lambda_1\mathscr{K}\Lambda_1)\Lambda_1$.

Using equation (6*b*), (2*a*)–(2*f*) and equations (9*b*), (A1.11*b*) of I and with $\omega_{ab} \equiv \omega_a - \omega_b$, we find that

$$\langle\langle \alpha i^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1)\Lambda_1|\beta j^{\dagger}\rangle\rangle$$
$$= z\delta_{\alpha\beta}\delta_{ij} - \langle\langle \alpha i^{\dagger}|\mathcal{K}|\beta j^{\dagger}\rangle\rangle$$
$$= z\delta_{\alpha\beta}\delta_{ij} - \langle\alpha|K|\beta\rangle\delta_{ij} + \langle i|K|j\rangle^{*}\delta_{\alpha\beta}$$
$$= (z-\hbar\omega_{\alpha i})\delta_{\alpha\beta}\delta_{ij} - \hbar v_{\alpha\beta}\delta_{ij} + \hbar v_{ij}^{*}\delta_{\alpha\beta} \tag{12a}$$

$$\langle\langle \alpha i^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1)\Lambda_1|j\beta^{\dagger}\rangle\rangle = 0 \tag{12b}$$

$$\langle\langle i\alpha^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1)\Lambda_1|\beta j^{\dagger}\rangle\rangle = 0 \tag{12c}$$

$$\langle\langle i\alpha^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1)\Lambda_1|j\beta^{\dagger}\rangle\rangle = (z-\hbar\omega_{i\alpha})\delta_{\alpha\beta}\delta_{ij} + \hbar v_{\alpha\beta}^{*}\delta_{ij} - \hbar v_{ij}\delta_{\alpha\beta}. \tag{12d}$$

We now make the further approximation of neglecting the effect of the matrix elements v_{ij}, $v_{\alpha\beta}$. This amounts to calculating the matrix elements of $\Lambda_0\mathcal{R}^0\Lambda_0$ correct to the zeroth order in these quantities. With this approximation we find that the only non-zero matrix elements of $\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1-\Lambda_2\mathcal{K}_R\Lambda_2)^{-1}$ are given by

$$\langle\langle \alpha k^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1-\Lambda_2\mathcal{K}_R\Lambda_2)^{-1}\Lambda_1|\alpha k^{\dagger}\rangle\rangle = (z-\hbar\omega_{\alpha k})^{-1} \tag{13a}$$

$$\langle\langle k\alpha^{\dagger}|\Lambda_1(z-\Lambda_1\mathcal{K}\Lambda_1-\Lambda_2\mathcal{K}_R\Lambda_2)^{-1}\Lambda_1|k\alpha^{\dagger}\rangle\rangle = (z-\hbar\omega_{k\alpha})^{-1}. \tag{13b}$$

Hence using equations (10), (13), (9*a*), (9*b*), (9*c*) and (9*d*) we obtain the result

$$\langle\langle ij^{\dagger}|\Lambda_0\mathcal{R}^0(\hbar\omega)\Lambda_0|lm^{\dagger}\rangle\rangle = \hbar\sum_{\alpha}\left(\frac{v_{i\alpha}v_{l\alpha}^{*}\delta_{jm}}{\omega-\omega_{\alpha j}} + \frac{v_{j\alpha}^{*}v_{m\alpha}\delta_{il}}{\omega-\omega_{i\alpha}}\right). \tag{14}$$

Using equation (22*a*) of I and on completing the contour in the lower half-plane we then get

$$\langle\langle ij^{\dagger}|\Lambda_0 R^0(\tau)\Lambda_0|lm^{\dagger}\rangle\rangle$$
$$= -\mathrm{i}\hbar\sum_{\alpha}\left[v_{i\alpha}v_{l\alpha}^{*}\delta_{jm}\exp(-\mathrm{i}\omega_{\alpha j}\tau) + v_{j\alpha}^{*}v_{m\alpha}\delta_{il}\exp(-\mathrm{i}\omega_{i\alpha}\tau)\right] \qquad \tau \geq 0. \tag{15}$$

We can now examine conditions under which the Markoff approximation can be made. Suppose the matrix elements $v_{i\alpha}$ are similar in size over a range of continuum angular frequencies. We could then model $v_{i\alpha}$ in the form

$$v_{i\alpha} = \frac{v(i\Delta_c)}{(\omega_\alpha-\omega_c)+i\Delta_c}. \tag{16}$$

In this equation v is an effective strength factor, ω_c a suitable frequency in the middle of the continuum, Δ_c an effective bandwidth for the matrix elements $v_{i\alpha}$ ($\Delta_c \leq \omega_c$).

Writing Σ_α in the form $\int d\omega_\alpha \rho(\omega_\alpha)$, where $\rho(\omega_\alpha)$ is the density of continuum states (per unit angular frequency), a straightforward evaluation of a typical matrix element for $\Lambda_0 R^0(\tau)\Lambda_0$ gives

$$\langle\langle ij^{\dagger}|\Lambda_0 R^0(\tau)\Lambda_0|lm^{\dagger}\rangle\rangle \sim -\mathrm{i}\pi\hbar v^2\Delta_c\rho(\omega_c)\exp(-\mathrm{i}\omega_{cj}\tau)\exp(-\Delta_c\tau). \tag{17}$$

Thus we see that the correlation time is of order $1/\Delta_c$, which can be quite small. Hence the Markoff approximation can be valid when the coupling matrix element from the discrete states to the continuum states is spread over a wide band of continuum states.

Assuming the Markoff approximation is valid we next evaluate the Markovian relaxation matrix element $\langle\langle ij^\dagger|\Gamma^0|lm^\dagger\rangle\rangle$, where Γ^0 is given by equation (49) of I.

In evaluating the matrix elements of $\Lambda_0(\hbar\omega - i\hbar\varepsilon - \mathcal{K})^{-1}\Lambda_0$ we use an analogous technique to the derivation of equations (12), (13) and make the similar approximation of neglecting the effect of the matrix elements v_{ij}. We find that the only non-zero matrix elements are given as

$$\langle\langle lm^\dagger|\Lambda_0(\hbar\omega - i\hbar\varepsilon - \mathcal{K})^{-1}\Lambda_0|lm^\dagger\rangle\rangle = (\hbar\omega - i\hbar\varepsilon - \hbar\omega_{lm})^{-1}. \tag{18}$$

The contour integral in equation (49) of I is completed in the upper half-plane and we find that

$$\langle\langle ij^\dagger|\Gamma^0|lm^\dagger\rangle\rangle = \frac{1}{i\hbar}\langle\langle ij^\dagger|\Lambda_0\mathcal{R}^0(\hbar(\omega_{lm} + i\varepsilon))\Lambda_0|lm^\dagger\rangle\rangle. \tag{19}$$

Substituting from equation (14) we obtain the weak-coupling, zeroth-order expression (20) for the Markovian relaxation matrix elements.

$$\langle\langle ij^\dagger|\Gamma^0|lm^\dagger\rangle\rangle = -i\sum_\alpha\left(\frac{v_{i\alpha}v^*_{l\alpha}\delta_{jm}}{\omega_{l\alpha} + i\varepsilon} + \frac{v^*_{j\alpha}v_{m\alpha}\delta_{il}}{\omega_{\alpha m} + i\varepsilon}\right) \tag{20a}$$

$$\equiv \Gamma_{ij,lm}. \tag{20b}$$

Taking the scalar product with $|ij^\dagger\rangle\rangle$ of each side of the Markovian master equation (48) of I, using equations (A1.5*f*), (A1.11*b*), (9*b*) of I and equations (1), (2) and (6*a*) we find that

$$\frac{d}{dt}\rho_{ij} = -i\omega_{ij}\rho_{ij} - i\sum_l(v_{il}\rho_{lj} - \rho_{il}v_{lj}) + \sum_{lm}\Gamma_{ij,lm}\rho_{lm}. \tag{21}$$

Finally, to see whether the Markoff approximation is valid we calculate a typical relaxation matrix element $\Gamma_{ij,lm}$ in terms of our model for the $v_{i\alpha}$, as given by equation (16). We find that

$$\Gamma_{ij,lm} \sim \pi v^2\rho(\omega_c). \tag{22}$$

The condition $\Gamma\tau_c \ll 1$ which leads to the Markoff approximation being valid then becomes

$$\pi v^2\rho(\omega_c)/\Delta_c \ll 1. \tag{23}$$

This condition may often easily be satisfied. For example in autoionisation $2\pi v^2\rho(\omega_c)$, which is the Fermi golden rule rate constant for autoionisation (see below), may be about $10^{12}\ s^{-1}$ or less. On the other hand Δ_c may be of the order $10^{15}\ s^{-1}$, so that the left-hand side of equation (23) is of the order 10^{-3}.

3.2. *Single discrete state coupled to continuum states*

In this case, using equation (7) and including any non-zero v_{11} as part of ω_1 we have

$$v_{11} = 0 \tag{24a}$$

$$\rho_{11}(0) = 1. \tag{24b}$$

The single non-zero Markovian relaxation matrix element can be obtained from equation (20*a*). We find that

$$\Gamma_{11,11} = -2\pi \sum_{\alpha} |v_{1\alpha}|^2 \frac{\varepsilon/\pi}{\omega_{\alpha 1}^2 + \varepsilon^2}$$

$$= -2\pi\rho(\omega_1)|v_{1\alpha}|^2_{\omega_\alpha=\omega_1} \tag{25a}$$

$$= -\gamma_1. \tag{25b}$$

γ_1 is the Fermi golden rule rate constant for bound to continuum transitions.

The population of the single level ρ_{11} is then obtained from equation (21) and we have

$$\dot{\rho}_{11} = -\gamma_1\rho_{11}. \tag{26}$$

This describes the expected exponential decay of the population with a rate constant γ_1.

3.3. *Two coupled discrete states, one also coupled to continuum states*

Assuming that the system is initially in state $|1\rangle$, that state $|2\rangle$ only is coupled to the continuum states and that any non-zero v_{11} or v_{22} have been included in ω_1, ω_2 respectively, we then have

$$v_{11} = v_{22} = 0 \tag{27a}$$

$$v_{1\alpha} = 0 \tag{27b}$$

$$\rho_{11}(0) = 1 \tag{27c}$$

$$\rho_{12}(0) = \rho_{21}(0) = \rho_{22}(0) = 0. \tag{27d}$$

The non-zero Markovian relaxation matrix elements can be obtained from equation (20*a*) and are given by

$$\Gamma_{22,22} = -2\pi\rho(\omega_2)|v_{2\alpha}|^2_{\omega_\alpha=\omega_2} \tag{28a}$$

$$= -\gamma_2 \tag{28b}$$

$$\Gamma_{12,12} = -\mathrm{i}\sum_{\alpha} \frac{|v_{2\alpha}|^2}{\omega_{\alpha 2} + \mathrm{i}\varepsilon} \tag{28c}$$

$$= -\mathrm{i}\int \mathrm{d}\omega_\alpha \frac{P}{\omega_{\alpha 2}} \rho(\omega_\alpha)|v_{2\alpha}|^2 - \pi\rho(\omega_2)|v_{2\alpha}|^2_{\omega_\alpha=\omega_2} \tag{28d}$$

$$= -\mathrm{i}\Delta_{12} - \tfrac{1}{2}\gamma_2 \tag{28e}$$

$$\Gamma_{21,21} = \mathrm{i}\Delta_{12} - \tfrac{1}{2}\gamma_2. \tag{28f}$$

γ_2 is the Fermi golden rule rate constant for transition from state $|2\rangle$ to the continuum states. Δ_{12} is a shift of the zeroth-order transition frequency ω_{12}, as can be seen from its location in equations (29).

The populations and coherences of the two states can then be obtained from equation (21), and we have

$$\dot{\rho}_{11} = \mathrm{i}v_{12}^*\rho_{12} - \mathrm{i}v_{12}\rho_{21} \tag{29a}$$

$$\dot{\rho}_{12} = -\mathrm{i}(\omega_{12} + \Delta_{12} - \tfrac{1}{2}\mathrm{i}\gamma_2)\rho_{12} - \mathrm{i}v_{12}(\rho_{22} - \rho_{11}) \tag{29b}$$

$$\dot{\rho}_{21} = \mathrm{i}(\omega_{12} + \Delta_{12} + \tfrac{1}{2}\mathrm{i}\gamma_2)\rho_{21} + \mathrm{i}v_{12}^*(\rho_{22} - \rho_{11}) \tag{29c}$$

$$\dot{\rho}_{22} = -\mathrm{i}v_{12}^*\rho_{12} + \mathrm{i}v_{12}\rho_{21} - \gamma_2\rho_{22}. \tag{29d}$$

These equations can easily be solved by Laplace transform methods. We find that

$$\rho_{11}(t) = \left|\frac{a \sin\frac{1}{2}\Omega t - \mathrm{i}\,\Omega \cos\frac{1}{2}\Omega t}{\Omega}\right|^2 \exp(-\tfrac{1}{2}\gamma_2 t) \tag{30a}$$

$$\rho_{22}(t) = 4|v_{12}|^2 \left|\frac{\sin\frac{1}{2}\Omega t}{\Omega}\right|^2 \exp(-\tfrac{1}{2}\gamma_2 t) \tag{30b}$$

$$a = -(\omega_{12} + \Delta_{12}) - \tfrac{1}{2}\mathrm{i}\gamma_2 \tag{30c}$$

$$\Omega = [(\omega_{12} + \Delta_{12} + \tfrac{1}{2}\mathrm{i}\gamma_2) + 4|v_{12}|^2]^{1/2}. \tag{30d}$$

In the case where $\omega_{12} + \Delta_{12}$ is small (resonance), then if the coupling matrix element v_{12} is large compared with the decay constant γ_2, the populations ρ_{11}, ρ_{22} exhibit damped oscillatory behaviour (Rabi oscillations). Results equivalent to equation (30) have been obtained by Knight (1977) in the case of resonant two-photon ionisation, which is a specific example of the situation dealt with here.

4. Population of reservoir states

4.1. *Case of two coupled discrete states, one also coupled to continuum states*

Using equations (A1.5*f*), (11) of I and equations (6*c*), (7) the population of the continuum state $|\alpha\rangle$ is given by

$$\begin{aligned}\rho_{\alpha\alpha}(t) &= \langle\!\langle \alpha\alpha^\dagger|\rho\rangle\!\rangle \\ &= \langle\!\langle \alpha\alpha^\dagger|\Lambda_2|\rho\rangle\!\rangle \\ &= \frac{\hbar}{2\pi\mathrm{i}}\sum_{ij}\int_c \mathrm{d}\omega\ \mathrm{e}^{-\mathrm{i}\omega t}\langle\!\langle \alpha\alpha^\dagger|\Lambda_2\mathscr{G}(\hbar\omega)\Lambda_0|ij^\dagger\rangle\!\rangle\rho_{ij}(0).\end{aligned} \tag{31}$$

Since case B applies, equation (40) in the general theory paper I then gives

$$\langle\!\langle \alpha\alpha^\dagger|\Lambda_2\mathscr{G}\Lambda_0|ij^\dagger\rangle\!\rangle = \langle\!\langle \alpha\alpha^\dagger|\Lambda_2\mathscr{G}^2\Lambda_2\Lambda_2\mathscr{V}\Lambda_1\Lambda_1\mathscr{G}^1\Lambda_1\Lambda_1\mathscr{V}^1\Lambda_0\Lambda_0\mathscr{G}^0\Lambda_0|ij^\dagger\rangle\!\rangle. \tag{32}$$

Rather than evaluate the population $\rho_{\alpha\alpha}(t)$ in general, we shall confine ourselves to the case considered in § 3.3, and also examine the population $\rho_{\alpha\alpha}(t)$ only in the regime where t is large. We thus need only consider equation (32) for the case $i = j = 1$.

We first consider $\Lambda_2\mathscr{G}^2\Lambda_2$, and hence $\Lambda_2\mathscr{R}^2\Lambda_2$. Using equations (8*a*), (6*g*), (8*c*) we find that

$$\Lambda_2\mathscr{R}^2(z)\Lambda_2 = 0 \tag{33a}$$

$$\Lambda_2\mathscr{G}^2(z)\Lambda_2 = \Lambda_2(z - \mathscr{H})^{-1}\Lambda_2 \tag{33b}$$

$$\Lambda_2(z - \mathscr{H})^{-1}\Lambda_2\Lambda_2(z - \mathscr{H}_\mathrm{R})\Lambda_2 = \Lambda_2. \tag{33c}$$

In calculating the non-zero matrix elements of $\Lambda_2(z - \mathscr{H})^{-1}\Lambda_2$ we make the same approximation used earlier of neglecting the contributions from the $v_{\alpha\beta}$ terms. We then find that the non-zero matrix elements of $\Lambda_2\mathscr{G}^2\Lambda_2$ are

$$\langle\!\langle \alpha\beta^\dagger|\Lambda_2\mathscr{G}^2(z)\Lambda_2|\alpha\beta^\dagger\rangle\!\rangle = (z - \hbar\omega_{\alpha\beta})^{-1}. \tag{34}$$

Using equation (34), the non-zero matrix elements of $\Lambda_2\mathscr{V}\Lambda_1$ from equations (9*g*), (9*h*) and (27*b*), we obtain

$$\langle\!\langle \alpha\alpha^\dagger|\Lambda_2\mathscr{G}(z)\Lambda_0|11^\dagger\rangle\!\rangle = (\hbar/z)(-v_{2\alpha}\langle\!\langle \alpha 2^\dagger|\Lambda_1\mathscr{G}^1(z)\Lambda_1\Lambda_1\mathscr{V}\Lambda_0\Lambda_0\mathscr{G}^0(z)\Lambda_0|11^\dagger\rangle\!\rangle$$
$$+v_{2\alpha}^*\langle\!\langle 2\alpha^\dagger|\Lambda_1\mathscr{G}^1(z)\Lambda_1\Lambda_1\mathscr{V}\Lambda_0\Lambda_0\mathscr{G}^0(z)\Lambda_0|11^\dagger\rangle\!\rangle). \tag{35}$$

We next consider $\Lambda_1\mathscr{G}^1\Lambda_1$ and hence $\Lambda_1\mathscr{R}^1\Lambda_1$. Using equation (45) of I and equation (8*a*), and making the same approximation for the matrix elements of $\Lambda_2\mathscr{G}^2\Lambda_2$ as involved in equation (34), we find that

$$\Lambda_1\mathscr{R}^1(z)\Lambda_1 = \sum_{\gamma\delta}\frac{\Lambda_1\mathscr{V}\Lambda_2|\gamma\delta^\dagger\rangle\!\rangle\langle\!\langle\gamma\delta^\dagger|\Lambda_2\mathscr{V}\Lambda_1}{z-\hbar\omega_{\gamma\delta}}. \tag{36}$$

Using equations (9*e*), (9*f*), (9*g*), (9*h*) and (27*b*) for the non-zero matrix elements of $\Lambda_1\mathscr{V}\Lambda_2$ and $\Lambda_2\mathscr{V}\Lambda_1$ we find the following non-zero matrix elements of $\Lambda_1\mathscr{R}^1(z)\Lambda_1$

$$\langle\!\langle\alpha 2^\dagger|\Lambda_1\mathscr{R}^1(z)\Lambda_1|\alpha 2^\dagger\rangle\!\rangle = \hbar^2\sum_\delta\frac{|v_{2\delta}|^2}{z-\hbar\omega_{\alpha\delta}} \tag{37a}$$

$$\langle\!\langle\alpha 2^\dagger|\Lambda_1\mathscr{R}^1(z)\Lambda_1|2\beta^\dagger\rangle\!\rangle = -\hbar^2\frac{v_{2\beta}^*v_{2\alpha}^*}{z-\hbar\omega_{\alpha\beta}} \tag{37b}$$

$$\langle\!\langle 2\alpha^\dagger|\Lambda_1\mathscr{R}^1(z)\Lambda_1|\beta 2^\dagger\rangle\!\rangle = -\hbar^2\frac{v_{2\beta}v_{2\alpha}}{z-\hbar\omega_{\beta\alpha}} \tag{37c}$$

$$\langle\!\langle 2\alpha^\dagger|\Lambda_1\mathscr{R}^1(z)\Lambda_1|2\alpha^\dagger\rangle\!\rangle = \hbar^2\sum_\delta\frac{|v_{2\delta}|^2}{z-\hbar\omega_{\delta\alpha}}. \tag{37d}$$

From an equation analogous to (A2.11) of I we see that the matrix elements of $\Lambda_1\mathscr{G}^1\Lambda_1$ are obtained by taking the inverse of the matrix for $\Lambda_1(z-\mathscr{H}-\Lambda_1\mathscr{R}^1(z)\Lambda_1)\Lambda_1$. Using equations (37), (1), (2*a*)–(2*e*) and equations (9*b*), (A1.11*b*) of I we find that

$$\langle\!\langle\alpha i^\dagger|\Lambda_1(z-\mathscr{H}-\Lambda_1\mathscr{R}^1(z)\Lambda_1)\Lambda_1|\beta j^\dagger\rangle\!\rangle$$
$$=(z-\hbar\omega_{\alpha i})\delta_{\alpha\beta}\delta_{ij}-\hbar v_{\alpha\beta}\delta_{ij}+\hbar v_{ij}^*\delta_{\alpha\beta}-\delta_{\alpha\beta}\hbar^2\delta_{i2}\delta_{j2}\sum_\delta\frac{|v_{2\delta}|^2}{z-\hbar\omega_{\alpha\delta}} \tag{38a}$$

$$\langle\!\langle\alpha i^\dagger|\Lambda_1(z-\mathscr{H}-\Lambda_1\mathscr{R}^1(z)\Lambda_1)\Lambda_1|j\beta^\dagger\rangle\!\rangle = \hbar^2\delta_{i2}\delta_{j2}\frac{v_{2\beta}^*v_{2\alpha}^*}{z-\hbar\omega_{\alpha\beta}} \tag{38b}$$

$$\langle\!\langle i\alpha^\dagger|\Lambda_1(z-\mathscr{H}-\Lambda_1\mathscr{R}^1(z)\Lambda_1)\Lambda_1|\beta j^\dagger\rangle\!\rangle = \hbar^2\delta_{i2}\delta_{j2}\frac{v_{2\beta}v_{2\alpha}}{z-\hbar\omega_{\beta\alpha}} \tag{38c}$$

$$\langle\!\langle i\alpha^\dagger|\Lambda_1(z-\mathscr{H}-\Lambda_1\mathscr{R}^1(z)\Lambda_1)\Lambda_1|j\beta^\dagger\rangle\!\rangle$$
$$=(z-\hbar\omega_{i\alpha})\delta_{ij}\delta_{\alpha\beta}-\hbar v_{ij}\delta_{\alpha\beta}+\hbar v_{\alpha\beta}^*\delta_{ij}-\delta_{\alpha\beta}\hbar^2\delta_{i2}\delta_{j2}\sum_\delta\frac{|v_{2\delta}|^2}{z-\hbar\omega_{\delta\alpha}}. \tag{38d}$$

To proceed further we make three more approximations. Firstly we neglect all matrix elements $v_{\alpha\beta}$, as in earlier approximations. Secondly, we ignore the off-diagonal matrix elements given by equations (38*b*) and (38*c*). This can be justified by showing that the corrections due to their presence are of higher order. Thirdly, we make the so-called pole approximation in which the z dependence of the sums over δ in equations (37*a*) and (37*d*) is ignored and z replaced by the values $\hbar\omega_{\alpha i}+i\hbar\varepsilon$ and

$\hbar\omega_{i\alpha}+i\hbar\varepsilon$ respectively. These correspond to values of z on the contour c closest to the poles of the matrix elements of $\Lambda_1\mathscr{G}^1\Lambda_1$.

The validity of the pole approximation can be established in several ways. Firstly, direct calculations of the sums over δ occurring in equations (37a), (37c) for specific models of the matrix elements $v_{2\delta}$ do, in fact, produce results which show only a weak dependence on z. Davis (1980) has evaluated such expressions for electric dipole matrix elements between bound and continuum states in hydrogenic atoms. Secondly, the expressions (37a), (37d) are essentially the same as the matrix elements of $\Lambda_0\mathscr{R}^0(z)\Lambda_0$ given in equations (14). These are weakly dependent on z in the situation considered here in which the Markoff approximation applies, since the Laplace transform of the latter expressions yields the matrix elements of the relaxation operator, and these decay to zero over very short time scales τ_c. Thus, at the fundamental level, the pole approximation is implied by the Markoff approximation and vice versa.

Using the pole approximation and equation (28) we then have

$$\sum_\delta \frac{|v_{2\delta}|^2}{z-\hbar\omega_{\alpha\delta}} \doteqdot \frac{1}{\hbar}(\Delta_{12}-\tfrac{1}{2}\mathrm{i}\gamma_2) \tag{39a}$$

$$\sum_\delta \frac{|v_{2\delta}|^2}{z-\hbar\omega_{\delta\alpha}} \doteqdot \frac{1}{\hbar}(-\Delta_{12}-\tfrac{1}{2}\mathrm{i}\gamma_2). \tag{39b}$$

Using the last three approximations and substituting equations (39) and (27a) into equations (38) we see that

$$\begin{bmatrix} \langle\!\langle \alpha 1^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|\alpha 1^\dagger\rangle\!\rangle & \langle\!\langle \alpha 1^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|\alpha 2^\dagger\rangle\!\rangle \\ \langle\!\langle \alpha 2^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|\alpha 1^\dagger\rangle\!\rangle & \langle\!\langle \alpha 2^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|\alpha 2^\dagger\rangle\!\rangle \end{bmatrix} \begin{bmatrix} z-\hbar\omega_{\alpha 1} & \hbar v_{12}^* \\ \hbar v_{12} & z-\hbar\bar{\omega}_{\alpha 2}+\frac{1}{2}\mathrm{i}\hbar\gamma_2 \end{bmatrix} = E_2 \tag{40a}$$

$$\begin{bmatrix} \langle\!\langle 1\alpha^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|1\alpha^\dagger\rangle\!\rangle & \langle\!\langle 1\alpha^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|2\alpha^\dagger\rangle\!\rangle \\ \langle\!\langle 2\alpha^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|1\alpha^\dagger\rangle\!\rangle & \langle\!\langle 2\alpha^\dagger|\Lambda_1\mathscr{G}^1\Lambda_1|2\alpha^\dagger\rangle\!\rangle \end{bmatrix} \begin{bmatrix} z-\hbar\omega_{1\alpha} & -\hbar v_{12} \\ -\hbar v_{12}^* & z+\hbar\bar{\omega}_{\alpha 2}+\frac{1}{2}\mathrm{i}\hbar\gamma_2 \end{bmatrix} = E_2. \tag{40b}$$

The quantity $\bar{\omega}_{\alpha 2}$ is defined as

$$\bar{\omega}_{\alpha 2}=\omega_{\alpha 2}+\Delta_{12}. \tag{41}$$

E_n is the $n\times n$ unit matrix.

The matrix elements of $\Lambda_1\mathscr{G}^1\Lambda_1$ are then determined from equations (40). Substituting the result into equation (35), then using the non-zero matrix elements of $\Lambda_1\mathscr{V}\Lambda_0$ from equations (9c) and (9d), we obtain the following results for the resolvent matrix element

$$\begin{aligned} &\langle\!\langle \alpha\alpha^\dagger|\Lambda_2\mathscr{G}(\hbar\omega)\Lambda_0|11^\dagger\rangle\!\rangle \\ &\quad=\frac{|v_{2\alpha}|^2}{\omega}\bigg[\frac{v_{12}}{f_\alpha(\omega)}\langle\!\langle 21^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\!\rangle \\ &\qquad-\frac{v_{12}^*}{f_\alpha(-\omega^*)^*}\langle\!\langle 12^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\!\rangle \\ &\qquad-\bigg(\frac{(\omega-\omega_{\alpha 1})}{f_\alpha(\omega)}+\frac{(\omega+\omega_{\alpha 1})}{f_\alpha(-\omega^*)^*}\bigg)\langle\!\langle 22^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\!\rangle\bigg]. \end{aligned} \tag{42}$$

The quantity $f_\alpha(\omega)$ is defined as

$$f_\alpha(\omega)=(\omega-\omega_{\alpha 1})(\omega-\bar{\omega}_{\alpha 2}+\tfrac{1}{2}\mathrm{i}\gamma_2)-|v_{12}|^2. \tag{43}$$

Next we need to determine the matrix elements of $\Lambda_0\mathscr{G}^0\Lambda_0$ and hence of $\Lambda_0\mathscr{R}^0\Lambda_0$. This calculation has been done in § 3.1, within certain approximations discussed therein, and yields the result given in equation (14).

From equations (8*d*), (1*b*), (2*a*), (2*b*), (2*c*) and equations (A2.11), (9*b*), (A1.11*b*) of I we find that

$$\sum_{kl}\langle\langle ij^\dagger|\Lambda_0\mathscr{G}^0(z)\Lambda_0|kl^\dagger\rangle\rangle\begin{Bmatrix}(z-\hbar\omega_{kl})\delta_{km}\delta_{ln}-\hbar v_{km}\delta_{ln}+\hbar v^*_{ln}\delta_{km}\\ -\langle\langle kl^\dagger|\Lambda_0\mathscr{R}^0(z)\Lambda_0|mn^\dagger\rangle\rangle\end{Bmatrix}=\delta_{im}\delta_{jn}. \tag{44}$$

Substituting for the matrix elements of $\Lambda_0\mathscr{R}^0\Lambda_0$ from equation (14), using the pole approximation and equation (27*a*), we find that

$$(\langle\langle ij^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|lm^\dagger\rangle\rangle)_{\text{Matrix}}$$

$$=\frac{1}{\hbar}\times\begin{array}{c} \\ 11^\dagger \\ 12^\dagger \\ 21^\dagger \\ 22^\dagger\end{array}\begin{array}{c}\begin{array}{cccc}11^\dagger & 12^\dagger & 21^\dagger & 22^\dagger\end{array}\\ \begin{bmatrix}\omega & v^*_{12} & -v_{12} & 0\\ v_{12} & \omega-\bar{\omega}_{12}+\frac{1}{2}\mathrm{i}\gamma_2 & 0 & -v_{12}\\ -v^*_{12} & 0 & \omega+\bar{\omega}_{12}+\frac{1}{2}\mathrm{i}\gamma_2 & v^*_{12}\\ 0 & -v^*_{12} & v_{12} & \omega+\mathrm{i}\gamma_2\end{bmatrix}^{-1}\end{array}. \tag{45}$$

The quantity $\bar{\omega}_{12}$ is defined as

$$\bar{\omega}_{12}=\omega_{12}+\Delta_{12}. \tag{46}$$

We note that the matrix given in equation (45) is exactly that involved in obtaining the Laplace transform solution of the master equations (29).

Inverting the last matrix we find that

$$\langle\langle 12^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\rangle=\frac{1}{\hbar}\,\frac{v^*_{12}(\omega+\mathrm{i}\gamma_2)(\omega-\bar{\omega}_{12}+\frac{1}{2}\mathrm{i}\gamma_2)}{g(\omega)} \tag{47a}$$

$$\langle\langle 21^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\rangle=\frac{-1}{\hbar}\,\frac{v_{12}(\omega+\mathrm{i}\gamma_2)(\omega+\bar{\omega}_{12}+\frac{1}{2}\mathrm{i}\gamma_2)}{g(\omega)} \tag{47b}$$

$$\langle\langle 22^\dagger|\Lambda_0\mathscr{G}^0(\hbar\omega)\Lambda_0|11^\dagger\rangle\rangle=\frac{-1}{\hbar}|v_{12}|^2\frac{(2\omega+\mathrm{i}\gamma_2)}{g(\omega)}. \tag{47c}$$

The quantity $g(\omega)$ is defined as

$$g(\omega)=\omega^4+\omega^3(2\mathrm{i}\gamma_2)-\omega^2(\tfrac{5}{4}\gamma_2^2+\bar{\omega}_{12}^2+4|v_{12}|^2)-\mathrm{i}\gamma_2\omega(\tfrac{1}{4}\gamma_2^2+\bar{\omega}_{12}^2+4|v_{12}|^2)+\gamma_2^2|v_{12}|^2. \tag{48}$$

$g(\omega)$ is similar to the Torrey polynomial.

Substituting the results for the matrix elements of $\Lambda_0\mathscr{G}^0\Lambda_0$ from equation (47) into the expression (42) we find that

$$\langle\langle\alpha\alpha^\dagger|\Lambda_2\mathscr{G}(\hbar\omega)\Lambda_0|11^\dagger\rangle\rangle$$

$$=\frac{|v_{2\alpha}|^2|v_{12}|^2}{\hbar\omega g(\omega)f_\alpha(\omega)f_\alpha(-\omega^*)^*}$$

$$\times\{f_\alpha(-\omega^*)^*[(\omega+\mathrm{i}\gamma_2)(\omega-\bar{\omega}_{12}+\tfrac{1}{2}\mathrm{i}\gamma_2)+(2\omega+\mathrm{i}\gamma_2)(\omega-\omega_{\alpha 1})]$$

$$+f_\alpha(\omega)[(\omega+\mathrm{i}\gamma_2)(\omega+\bar{\omega}_{12}+\tfrac{1}{2}\mathrm{i}\gamma_2)+(2\omega+\mathrm{i}\gamma_2)(\omega+\omega_{\alpha 1})]\}. \tag{49}$$

We note that there is a $1/\omega$ factor in the last expression, which shows that $\rho_{\alpha\alpha}(t)$ will approach a finite value as t becomes large.

The population of the continuum state $|\alpha\rangle$ is then calculated by substituting from equation (49) into equation (31), noting that $\rho_{11}(0)=1$ and all other $\rho_{ij}(0)$ are zero. The integral is evaluated by completing the contour in the lower half-plane. For large t the only contribution is from the pole $\omega=0$, and we find for t large that

$$\rho_{\alpha\alpha}(t)\simeq\frac{|v_{12}|^2|v_{2\alpha}|^2}{|((\bar{\omega}_{\alpha2}-\bar{\omega}_{12})(\bar{\omega}_{\alpha2}+\frac{1}{2}\mathrm{i}\gamma_2)-|v_{12}|^2)|^2}. \tag{50}$$

The important ω_α dependence is contained in the denominator rather than in the weakly varying quantity $v_{2\alpha}$. In general, a two-peak result can occur (Autler–Townes splitting), for example when the coupling term v_{12} becomes large in near resonance conditions ($\bar{\omega}_{12}\doteqdot 0$).

A result analogous to that in equation (50) has been obtained by Knight (1977) in discussing the spectrum of photoelectrons emitted in two-photon resonant ionisation. This situation is a special case of that considered here.

Finally, in order to give a specific example, the coupled master equations for $\Lambda_i|\rho\rangle\rangle$, $i\neq 0$, are given by equation (42) of I as

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_1|\rho(t)\rangle\rangle=\Lambda_1\mathscr{H}\Lambda_1\Lambda_1|\rho(t)\rangle\rangle+\int_0^t\mathrm{d}\tau\Lambda_1R(\tau)\Lambda_0\Lambda_0|\rho(t-\tau)\rangle\rangle \tag{51a}$$

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Lambda_2|\rho(t)\rangle\rangle=\Lambda_2\mathscr{H}\Lambda_2\Lambda_2|\rho(t)\rangle\rangle+\int_0^t\mathrm{d}\tau\,\Lambda_2R^1(\tau)\Lambda_1\Lambda_1|\rho(t-\tau)\rangle\rangle. \tag{51b}$$

Within the weak-coupling theory used there it can easily be shown that the non-zero matrix elements of the corresponding line shift operators are

$$\langle\langle\alpha1^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|21^\dagger\rangle\rangle=\frac{\hbar(\omega-\omega_{\alpha1})(\omega-\bar{\omega}_{\alpha2}+\frac{1}{2}\mathrm{i}\gamma_2)v_{\alpha2}}{f_\alpha(\omega)} \tag{52a}$$

$$\langle\langle\alpha1^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|22^\dagger\rangle\rangle=\frac{-\hbar(\omega-\omega_{\alpha1})v_{12}^*v_{\alpha2}}{f_\alpha(\omega)} \tag{52b}$$

$$\langle\langle\alpha2^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|21^\dagger\rangle\rangle=\frac{-\hbar(\omega-\omega_{\alpha2})v_{12}v_{\alpha2}}{f_\alpha(\omega)} \tag{52c}$$

$$\langle\langle\alpha2^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|22^\dagger\rangle\rangle=\frac{\hbar(\omega-\omega_{\alpha2})(\omega-\omega_{\alpha1})v_{\alpha2}}{f_\alpha(\omega)} \tag{52d}$$

$$\langle\langle1\alpha^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|12^\dagger\rangle\rangle=-\frac{\hbar(\omega-\omega_{1\alpha})(\omega+\bar{\omega}_{\alpha2}+\frac{1}{2}\mathrm{i}\gamma_2)v_{\alpha2}^*}{f_\alpha(-\omega^*)^*} \tag{52e}$$

$$\langle\langle1\alpha^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|22^\dagger\rangle\rangle=-\frac{\hbar(\omega-\omega_{1\alpha})v_{12}v_{\alpha2}^*}{f_\alpha(-\omega^*)^*} \tag{52f}$$

$$\langle\langle2\alpha^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|12^\dagger\rangle\rangle=-\frac{\hbar(\omega-\omega_{2\alpha})v_{12}^*v_{\alpha2}^*}{f_\alpha(-\omega^*)^*} \tag{52g}$$

$$\langle\langle2\alpha^\dagger|\Lambda_1\mathscr{R}^0(\hbar\omega)\Lambda_0|22^\dagger\rangle\rangle=-\frac{\hbar(\omega-\omega_{2\alpha})(\omega-\omega_{1\alpha})v_{\alpha2}^*}{f_\alpha(-\omega^*)^*} \tag{52h}$$

$$\langle\langle\alpha\beta^\dagger|\Lambda_2\mathscr{R}^1(\hbar\omega)\Lambda_1|\alpha i^\dagger\rangle\rangle=-\hbar v_{i\beta} \tag{52i}$$

$$\langle\langle \alpha\beta^{\dagger}|\Lambda_2\mathcal{R}^1(\hbar\omega)\Lambda_1|i\beta^{\dagger}\rangle\rangle = \hbar v^*_{i\alpha}. \tag{52j}$$

The relevant matrix elements of $\Lambda_1 \boldsymbol{R}^0(\tau)\Lambda_0$ and $\Lambda_2 \boldsymbol{R}^1(\tau)\Lambda_0$ can then be obtained via equation (20) of I. The latter expressions will not be written down here.

From results (52*a*)–(52*h*) it can be seen that the non-zero matrix elements of $\Lambda_1 \boldsymbol{R}^0(\tau)\Lambda_0$ decay to zero with a timescale of the order γ_2^{-1}, whereas from equations (52*i*), (52*j*) those of $\Lambda_2 \boldsymbol{R}^1(\tau)\Lambda_1$ have a Dirac delta function τ dependence. Hence $\Lambda_1|\rho\rangle\rangle$ satisfies a non-Markovian master equation, whilst $\Lambda_2|\rho\rangle\rangle$ satisfies a Markovian master equation, which illustrates the general point that some $\Lambda_i|\rho\rangle\rangle$ in a given problem may satisfy the Markoff approximation whilst other $\Lambda_i|\rho\rangle\rangle$ may not.

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