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A density matrix approach to problems in time-dependent perturbation theory

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Abstract. In the present paper it is demonstrated that the density matrix method may be applied to problems in time-dependent perturbation theory. The advantages of the method are that it is compact, systematic and the effects of radiation damping can be readily treated on a phenomenological basis.

1. Introduction

The standard method of evaluating the properties of a system subject to a time-dependent perturbation is of course time-dependent perturbation theory (Schiff 1968). However, the density matrix gives an equivalent description of the system (Fano 1964). Furthermore, as noted earlier (Stanton 19 1/2), if one is interested in evaluating entities to second and higher order in the perturbation, then the density matrix offers distinct advantages in that the method is simpler (i.e. no adiabatic switching is required and no integrals need be evaluated) and much quicker, and radiation damping effects can be readily incorporated in a phenomenological manner. Unfortunately the previous development (Stanton 1969) contains several formal errors and the resultant formulae for the hyper-Raman effect (Long and Stanton 1970) contain approximations and an incorrect treatment of damping effects. The purpose of the present paper is to correct these errors in the formalism and develop an alternative treatment in terms of which the effects of radiation damping can be correctly described. This is of importance since there is a vast literature on methods of evaluating the latter (Haake 1973, Louisell 1973).

2. Formalistic considerations

For many problems associated with nonlinear phenomena we are required to evaluate the following integral (Placzek 1938, Bloembergen and Shen 1964):

$$M'_{nk} = \langle\psi'_n|\boldsymbol{M}|\psi'_k\rangle \tag{2.1}$$

where $|\psi'_r\rangle$ is a (normalised) time-dependent state of the perturbed system and $\boldsymbol{M}$ is the dipole moment operator of this same system. The formal problem (Stanton 1969) could be stated simply as one of relating the matrix element in equation (2.1) to matrix elements of some 'equivalent operator' between the unperturbed states $|\psi_n\rangle$ and $|\psi_k\rangle$ of the original system. According to the earlier work (Stanton 1969) we can write in place of equation (2.1)

$$M'_{nk} = \langle\psi_n|\phi M\phi|\psi_k\rangle \tag{2.2}$$

where ϕ is a density matrix operator. Rather than discuss the inconsistencies of the previous formalism, we first present an alternative treatment which demonstrates that equation (2.2) is not valid.

The total Hamiltonian of the perturbed system is given by

$$H = H_0 + V$$

where H_0 is the Hamiltonian of the unperturbed system with eigenstates $|\psi_r\rangle$ i.e.

$$H_0|\psi_r\rangle = E_r|\psi_r\rangle = \mathrm{i}\hbar(\partial/\partial t)|\psi_r\rangle \tag{2.3}$$

The time-dependent perturbation V represents the interaction of the system with the incident electromagnetic radiation $\boldsymbol{E}$ of frequency ω, i.e.

$$V = -\boldsymbol{M}.\boldsymbol{E} \tag{2.4}$$

where

$$\boldsymbol{E} = \boldsymbol{F}\exp(-\mathrm{i}\omega t) + \boldsymbol{F}^*\exp(\mathrm{i}\omega t). \tag{2.5}$$

Expanding the perturbed states in terms of the unperturbed ones

$$|\psi'_r\rangle = \sum_s d_s|\psi_s\rangle \tag{2.6}$$

and introducing the operator $\phi_1(t)$ and its Hermitian conjugate $\phi_2(t)$ according to the prescription

$$\phi_1(t) = \sum_s |\psi_s\rangle\langle\psi'_s| \tag{2.7}$$

$$\phi_2(t) = \sum_r |\psi'_r\rangle\langle\psi_r| \tag{2.8}$$

we obtain, from the orthogonality and completeness relations,

$$M'_{nk} = \langle\psi_n|\phi_1(t)M\phi_2(t)|\psi_k\rangle \tag{2.9}$$

where

$$\phi_1(t)\phi_1^+(t) = \phi_2(t)\phi_2^+(t) = 1.$$

Since $\phi_1(0) = \phi_2(0) = 1$ we see that both $\phi_1(t)$ and $\phi_2(t)$ are unitary time development operators that bring the time-zero basis of eigenvectors to that at time t. Thus we have achieved the objective of expressing the dipole matrix element in terms of the unperturbed eigenstates. However, the expression in equation (2.9) is not identical to that in equation (2.2). Furthermore, and more importantly, we see from equation (2.7) that

$$\mathrm{i}\hbar\,\partial\phi_1/\partial t = [H_0, \phi_1] - \phi_1 V = [H, \phi_1] - V\phi_1. \tag{2.10}$$

Similarly

$$\mathrm{i}\hbar\,\partial\phi_2/\partial t = [H_0, \phi_2] + V\phi_2 = [H, \phi_2] + \phi_2 V. \tag{2.11}$$

This shows that neither ϕ_1 nor ϕ_2 can be regarded as density operators in the sense that they do not obey the Liouville–von Neumann equation (Fano 1964). Nonetheless, in the spirit of the approach introduced previously (Stanton 1969) they can be employed in a systematic manner for solving the problem under consideration. To this end we expand ϕ_1 and ϕ_2 as a power series in the perturbation denoted symbolically by the parameter λ:

$$\begin{aligned}\phi_1 &= \phi_1^{(0)} + \lambda\phi_1^{(1)} + \lambda^2\phi_1^{(2)} + \dots \\ \phi_2 &= \phi_2^{(0)} + \lambda\phi_2^{(1)} + \lambda^2\phi_2^{(2)} + \dots .\end{aligned} \tag{2.12}$$

The first equation in the resulting hierarchy for ϕ_1 (say) is then

$$\mathrm{i}\hbar\dot{\phi}_1^{(0)} = [H_0, \phi_1^{(0)}]$$

with the solution

$$\phi_1^{(0)} = \exp[(-\mathrm{i}/\hbar)H_0 t]\phi_1^{(0)}(0)\exp[(+\mathrm{i}/\hbar)H_0 t]. \tag{2.13}$$

Since the perturbation vanishes at $t=0$ we have from the definition of ϕ_1 in equation (2.7) that

$$\phi_1^{(0)}(0) = \sum_s |\psi_s(0)\rangle\langle\psi_s(0)| \equiv 1. \tag{2.14}$$

Similarly

$$\phi_2^{(0)}(0) = 1.$$

Thus from equation (2.9) the zero-order contribution to M'_{nk} is

$$\langle\psi_n|\boldsymbol{M}|\psi_k\rangle = \langle\phi_n|\boldsymbol{M}|\phi_k\rangle \exp(-\mathrm{i}\omega_{kn}t) \tag{2.15}$$

where

$$\omega_{kn} = (1/\hbar)(E_k - E_n).$$

The next equation in the hierarchy for ϕ_1 is

$$\mathrm{i}\hbar\dot{\phi}_1^{(1)} = [H_0, \phi_1^{(1)}] - \phi_1^{(0)}V = [H_0, \phi_1^{(1)}] - V. \tag{2.16}$$

Since the 'driving' term V contains two characteristic time dependences, we write

$$\phi_1^{(1)} = \phi_1^{(1)+} + \phi_1^{(1)-} \tag{2.17}$$

where

$$\phi_1^{(1)+} \propto \exp(\mathrm{i}\omega t)$$
$$\phi_1^{(1)-} \propto \exp(-\mathrm{i}\omega t).$$

Taking the $\langle\phi_l|\dots|\phi_m\rangle$ matrix element of equation (2.16), we obtain the two solutions

$$\phi_{1\,lm}^{(1)+} = -(\boldsymbol{M}\cdot\boldsymbol{F}^*)_{lm}\exp(\mathrm{i}\omega t)/\hbar(\omega_{lm}+\omega)$$

and

$$\phi_{1\,lm}^{(1)-} = -(\boldsymbol{M}\cdot\boldsymbol{F})_{lm}\exp(-\mathrm{i}\omega t)/\hbar(\omega_{lm}-\omega).$$

Similarly the two corresponding solutions for ϕ_2 are

$$\phi_{2\,lk}^{(1)+} = (\boldsymbol{M}\cdot\boldsymbol{F}^*)_{lk}\exp(\mathrm{i}\omega t)/\hbar(\omega_{lk}+\omega)$$

and

$$\phi_{2\,lk}^{(1)-} = (\boldsymbol{M}\cdot\boldsymbol{F})_{lk}\exp(-\mathrm{i}\omega t)/\hbar(\omega_{lk}-\omega).$$

Employing these results in equation (2.9) shows that the corresponding contribution to the transition moment M'_{nk} is

$$\sum_r (1/\hbar)\{[\boldsymbol{M}_{nr}(\boldsymbol{M}_{rk}\cdot\boldsymbol{F})/(\omega_{rk}-\omega)+(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rk}/(\omega_{rn}+\omega)]\exp[-\mathrm{i}(\omega_{kn}+\omega)t]$$
$$+[(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rk}/(\omega_{rn}-\omega)$$
$$+\boldsymbol{M}_{nr}(\boldsymbol{M}_{rk}\cdot\boldsymbol{F}^*)/(\omega_{rk}+\omega)]\exp[-\mathrm{i}(\omega_{kn}-\omega)t]\}. \qquad (2.18)$$

The expressions in equations (2.15) and (2.18) agree with known results (Placzek 1938) but are more concisely obtained. Since ϕ_1 and ϕ_2 do not obey the Liouville–von Neumann equation, it is not clear how the effects of radiation damping may be incorporated phenomenologically into the expressions. It is to overcome these problems that we introduce a simpler alternative formulation of the whole problem in the next section.

3. The density matrix approach

Tracing over an arbitrary complete set of states we find that the transition moment $\boldsymbol{M}'_{nk}$ can be written as

$$\boldsymbol{M}'_{nk}=\langle\psi'_n|\boldsymbol{M}|\psi'_k\rangle=\mathrm{Tr}|\psi'_k\rangle\langle\psi'_n|\boldsymbol{M}$$
$$=\mathrm{Tr}\, p\boldsymbol{M} \qquad (3.1)$$

where

$$p=|\psi'_k\rangle\langle\psi'_n|. \qquad (3.2)$$

Although p is traceless, i.e. $\mathrm{Tr}\, p=0$, it does satisfy the Liouville–von Neumann equation

$$\partial p/\partial t=(-\mathrm{i}/\hbar)[H,p] \qquad (3.3)$$

and as a consequence can be regarded as a density operator (Fano 1964). The problem is now solved in exactly the same manner as before by expanding p as a power series in the interaction parameter

$$p=p^{(0)}+\lambda p^{(1)}+\lambda^2 p^{(2)}+\ldots. \qquad (3.4)$$

This leads to the following hierarchy of equations:

$$\dot{p}^{(n)}=-(\mathrm{i}/\hbar)[H_0,p^{(n)}]-(\mathrm{i}/\hbar)[V,p^{(n-1)}]-\Gamma p^{(n)} \qquad (3.5)$$

where the effects of radiation damping have been included phenomenologically by adding, in the symbolic form, $-\Gamma p$ to the equation of motion.

The zero-order term is obtained from

$$\dot{p}^{(0)}=-(\mathrm{i}/\hbar)[H_0,p^{(0)}]$$

which gives

$$p^{(0)}(t)=\exp(-\mathrm{i}\omega_{kn}t)|\phi_k\rangle\langle\phi_n|. \qquad (3.6)$$

Hence the zero-order contribution to the transition moment is

$$\mathrm{Tr}\, p^{(0)}\boldsymbol{M}=\exp(-\mathrm{i}\omega_{kn}t)\,\mathrm{Tr}|\phi_k\rangle\langle\phi_n|\boldsymbol{M}$$
$$=\langle\phi_n|\boldsymbol{M}|\phi_k\rangle\exp(-\mathrm{i}\omega_{kn}t). \qquad (3.7)$$

First-order terms are obtained from

$$\dot{p}^{(1)} = -(\mathrm{i}/\hbar)[H_0, p^{(1)}] - (\mathrm{i}/\hbar)[V, p^{(0)}] - \Gamma p^{(1)}. \tag{3.8}$$

Considering the 'driving' term $-(\mathrm{i}/\hbar)[V, p^{(0)}]$ we have

$$\begin{aligned} -(\mathrm{i}/\hbar)[V, p^{(0)}] \\ &= (\mathrm{i}/\hbar)[\boldsymbol{M}.\boldsymbol{F}, p^{(0)}(0)] \exp[-\mathrm{i}(\omega_{kn}+\omega)t] \\ &\quad + \mathrm{i}/\hbar[\boldsymbol{M}.\boldsymbol{F}^*, p^{(0)}(0)] \exp[-\mathrm{i}(\omega_{kn}-\omega)t]. \end{aligned}$$

This shows that $p^{(1)}$ has two separate time components, i.e.

$$p^{(1)} = p^{(1)-}(t) + p^{(1)+}(t)$$

where

$$p^{(1)-}(t) \propto \exp[-\mathrm{i}(\omega_{kn}+\omega)t]$$

and

$$p^{(1)+}(t) \propto \exp[-\mathrm{i}(\omega_{kn}-\omega)t].$$

Taking the $\langle\phi_l|\ldots|\phi_m\rangle$ matrix element of equation (3.8) shows that for $p^{(1)-}$ we obtain

$$p_{lm}^{(1)-} = (1/\hbar)\sum_r \left[\frac{p_{lr}^{(0)}(\boldsymbol{M}_{rm}.\boldsymbol{F}) - (\boldsymbol{M}_{lr}.\boldsymbol{F})p_{rm}^{(0)}}{\omega_{kn}+\omega-\omega_{lm}+\mathrm{i}\Gamma_{lm}}\right]\exp(-\mathrm{i}\omega t). \tag{3.9}$$

But from equation (3.6) we have

$$p_{lr}^{(0)} = \langle\phi_l|p^{(0)}|\phi_r\rangle = \exp(-\mathrm{i}\omega_{kn}t)\delta_{lk}\delta_{nr}. \tag{3.10}$$

As a result the expression for $p_{lm}^{(1)-}$ becomes

$$p_{lm}^{(1)-} = (1/\hbar)\left[\frac{(\boldsymbol{M}_{nm}.\boldsymbol{F})\delta_{lk} - (\boldsymbol{M}_{lk}.\boldsymbol{F})\delta_{nm}}{\omega_{kn}-\omega_{lm}+\omega+\mathrm{i}\Gamma_{lm}}\right]\exp[-\mathrm{i}(\omega_{kn}+\omega)t]. \tag{3.11}$$

Similarly the corresponding expression for $p_{lm}^{(1)+}$ is

$$p_{lm}^{(1)+} = (1/\hbar)\left[\frac{(\boldsymbol{M}_{nm}.\boldsymbol{F}^*)\delta_{lk} - (\boldsymbol{M}_{lk}.\boldsymbol{F}^*)\delta_{nm}}{\omega_{kn}-\omega_{lm}-\omega+\mathrm{i}\Gamma_{lm}}\right]\exp[-(\omega_{kn}-\omega)t]. \tag{3.12}$$

These results show that the first-order contribution to the transition moment is

$$\begin{aligned} \mathrm{Tr}\, p^{(1)}\boldsymbol{M} &= \mathrm{Tr}\, p^{(1)-}\boldsymbol{M} + \mathrm{Tr}\, p^{(1)+}\boldsymbol{M} \\ &= \sum_r (1/\hbar)\left\{\left[\frac{\boldsymbol{M}_{nr}(\boldsymbol{M}_{rk}.\boldsymbol{F})}{\omega_{rk}-\omega-\mathrm{i}\Gamma_{rn}} + \frac{(\boldsymbol{M}_{nr}.\boldsymbol{F})\boldsymbol{M}_{rk}}{\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr}}\right]\exp[-\mathrm{i}(\omega_{kn}+\omega)t]\right. \\ &\quad \left. + \left[\frac{\boldsymbol{M}_{nr}(\boldsymbol{M}_{rk}.\boldsymbol{F}^*)}{\omega_{rk}+\omega-\mathrm{i}\Gamma_{rn}} + \frac{(\boldsymbol{M}_{nr}.\boldsymbol{F}^*)\boldsymbol{M}_{rk}}{\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr}}\right]\exp[-\mathrm{i}(\omega_{kn}-\omega)t]\right\}. \end{aligned} \tag{3.13}$$

These results are identical with those previously obtained (Placzek 1938) but modified so as to include damping effects. We note that the present method is simpler than the one in the previous section involving ϕ_1 and ϕ_2, since we have only to solve the one equation. Furthermore as we shall demonstrate below, the second-order contributions to the transition moment describing the hyper-Raman effect (Long and Stanton 1970) can be rapidly obtained.

The second-order equation in the hierarchy for p is

$$\dot{p}^{(2)} = (-\mathrm{i}/\hbar)[H_0, p^{(2)}] - (\mathrm{i}\hbar)[V, p^{(1)}] - \Gamma p^{(2)}. \tag{3.14}$$

In this case the 'driving' term is $-(\mathrm{i}/\hbar)[V, p^{(1)}]$ and we have

$$-(\mathrm{i}/\hbar)[V, p^{(1)}]$$
$$= (\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}, p^{(1)-}(0)]\exp[-\mathrm{i}(\omega_{kn}+2\omega)t]$$
$$+(\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}, p^{(1)+}(0)]\exp(-\mathrm{i}\omega_{kn}t)+(\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}^*, p^{(1)-}(0)]\exp(-\mathrm{i}\omega_{kn}t)$$
$$+(\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}^*, p^{(1)+}(0)]\exp[-i(\omega_{kn}-2\omega)t].$$

Thus $p^{(2)}$ has three separate time components, i.e.

$$p^{(2)}(t)=p^{(2)-2\omega}(t)+p^{(2)+2\omega}(t)+p^{(2)*}(t)$$

where

$$p^{(2)-2\omega}(t)\propto\exp[-\mathrm{i}(\omega_{kn}+2\omega)t]$$
$$p^{(2)+2\omega}(t)\propto\exp[-(\omega_{kn}-2\omega)t]$$
$$p^{(2)*}(t)\propto\exp(-\mathrm{i}\omega_{kn}t).$$

Considering the equation of motion for $p^{(2)*}$ gives

$$-\mathrm{i}\omega_{kn}p^{(2)*}=-(\mathrm{i}/\hbar)[H_0, p^{(2)*}]+(\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}, p^{(1)+}]\exp(-\mathrm{i}\omega t)$$
$$+(\mathrm{i}/\hbar)[\boldsymbol{M}\cdot\boldsymbol{F}^*, p^{(1)-}]\exp(\mathrm{i}\omega t)-\Gamma p^{(2)*}. \qquad (3.15)$$

Taking the $\langle\phi_l|\ldots|\phi_m\rangle$matrix element of equation (3.15), and using equations (3.11) and (3.12) for the matrix elements of $p^{(1)-}$ and $p^{(1)+}$ respectively, shows that the corresponding contribution of $p^{(2)*}$ to the second-order transition moment is

$$\mathrm{Tr}\, p^{(2)*}\boldsymbol{M}=(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rs}\cdot\boldsymbol{F})\boldsymbol{M}_{sk}}{(\omega_{sn}+\mathrm{i}\Gamma_{ks})(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(i)}$$

$$+(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rk}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{ns}}{(\omega_{sk}-\mathrm{i}\Gamma_{sn})(\omega_{rk}+\omega-\mathrm{i}\Gamma_{rn})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(ii)}$$

$$+(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rs}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{sk}}{(\omega_{sn}+\mathrm{i}\Gamma_{ks})(\omega_{sn}+\omega+i\Gamma_{kr})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(iii)}$$

$$+(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{sr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rk}\cdot\boldsymbol{F})\boldsymbol{M}_{ns}}{(\omega_{sk}-\mathrm{i}\Gamma_{sn})(\omega_{rk}-\omega-\mathrm{i}\Gamma_{rn})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(iv)}$$

$$+(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}}{(\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{sr})(\omega_{sk}+\omega-\mathrm{i}\Gamma_{sn})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(v)}$$

$$-(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F})(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rs}}{(\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{sr})(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(vi)}$$

$$+(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F})(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rs}}{(\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{sr})(\omega_{sk}-\omega-\mathrm{i}\Gamma_{sn})}\right]\exp(-\mathrm{i}\omega_{kn}t) \qquad \text{(vii)}$$

$$-(1/\hbar^2)\sum_r\sum_s\left[\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}}{(\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{sr})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})}\right]\exp(-\mathrm{i}\omega_{kn}t). \qquad \text{(viii)}$$

Adding together the terms (v) and (viii) we have

$$(1/\hbar^2)\sum_r\sum_s\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}}{(\omega_{sk}+\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})}\left[\frac{\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{kr}+\mathrm{i}\Gamma_{sn}}{\omega_{kn}-\omega_{sr}+\mathrm{i}\Gamma_{sr}}\right]\exp(-\mathrm{i}\omega_{kn}t).$$

In the limit of small damping this is approximately

$$(1/\hbar^2)\sum_r\sum_s[(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}/(\omega_{sk}+\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})]\exp(-\mathrm{i}\omega_{kn}t).$$

Similarly adding together terms (vi) and (vii) we obtain in the same limit of small damping

$$(1/\hbar^2)\sum_r\sum_s[(\boldsymbol{M}_{sk}\cdot\boldsymbol{F})(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rs}/(\omega_{sk}-\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})]\exp(-\mathrm{i}\omega_{kn}t).$$

Employing exactly the same procedure as illustrated above to determine the contributions of $p^{(2)-2\omega}$ and $p^{(2)+2\omega}$ shows that the second-order transition moment is, in the limit of small damping, given by

$$\begin{aligned}\mathrm{Tr}\,p^{(2)}\boldsymbol{M}=(1/\hbar^2)\Bigg\{&\sum_r\sum_s\Bigg[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rs}\cdot\boldsymbol{F})\boldsymbol{M}_{sk}}{(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})(\omega_{sn}+\omega+\mathrm{i}\Gamma_{ks})}\\
&+\frac{(\boldsymbol{M}_{sr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rk}\cdot\boldsymbol{F})\boldsymbol{M}_{ns}}{(\omega_{rk}-\omega-\mathrm{i}\Gamma_{rn})(\omega_{sk}-2\omega-\mathrm{i}\Gamma_{sn})}\\
&+\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F})(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}}{(\omega_{sk}-\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})}\Bigg]\exp[-\mathrm{i}(\omega_{kn}+2\omega)t]\\
&+\sum_r\sum_s\Bigg[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rs}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{sk}}{(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})(\omega_{sr}-2\omega+\mathrm{i}\Gamma_{ks})}+\frac{(\boldsymbol{M}_{sr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rk}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{ns}}{(\omega_{rk}+\omega-\mathrm{i}\Gamma_{rn})(\omega_{sk}+2\omega-\mathrm{i}\Gamma_{sn})}\\
&+\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rs}}{(\omega_{sk}+\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}-\omega+i\Gamma_{kr})}\Bigg]\exp[-\mathrm{i}(\omega_{kn}-2\omega)t]\\
&+\sum_r\sum_s\Bigg[\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rs}\cdot\boldsymbol{F})\boldsymbol{M}_{sk}}{(\omega_{sn}+\mathrm{i}\Gamma_{ks})(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})}+\frac{(\boldsymbol{M}_{sr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rk}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{ns}}{(\omega_{sk}-\mathrm{i}\Gamma_{sn})(\omega_{rk}+\omega-\mathrm{i}\Gamma_{rn})}\\
&+\frac{(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})(\boldsymbol{M}_{rs}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{sk}}{(\omega_{sn}+\mathrm{i}\Gamma_{ks})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})}+\frac{(\boldsymbol{M}_{sr}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{rk}\cdot\boldsymbol{F})\boldsymbol{M}_{ns}}{(\omega_{sk}-\mathrm{i}\Gamma_{sn})(\omega_{rk}-\omega-\mathrm{i}\Gamma_{rn})}\\
&+\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F}^*)(\boldsymbol{M}_{nr}\cdot\boldsymbol{F})\boldsymbol{M}_{rs}}{(\omega_{sk}+\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}+\omega+\mathrm{i}\Gamma_{kr})}\\
&+\frac{(\boldsymbol{M}_{sk}\cdot\boldsymbol{F})(\boldsymbol{M}_{nr}\cdot\boldsymbol{F}^*)\boldsymbol{M}_{rs}}{(\omega_{sk}-\omega-\mathrm{i}\Gamma_{sn})(\omega_{rn}-\omega+\mathrm{i}\Gamma_{kr})}\Bigg]\exp(-\mathrm{i}\omega_{kn}t)\Bigg\}.\end{aligned}\tag{3.16}$$

This expression corrects the damping terms given in an equivalent expression by other authors (Long and Stanton 1970).

4. Discussion and conclusion

In the above analysis we have shown that it is not possible to define an operator ϕ which is such that the transition moment M'_{nk} can be written in the form

$$M'_{nk}(=\langle\psi'_n|\boldsymbol{M}|\psi'_k\rangle)=\langle\psi_n|\phi\boldsymbol{M}\phi|\psi_k\rangle.$$

However, it is possible to define two entities ϕ_1 and ϕ_2 which are such that

$$M'_{nk}=\langle\psi_n|\phi_1\boldsymbol{M}\phi_2|\psi_k\rangle.$$

The corresponding equations of motion for ϕ_1 and ϕ_2 (see equations (2.21) and (2.22)) possessed a mixed character which show that neither ϕ_1 nor ϕ_2 can be regarded as a density operator. Nonetheless, by solving the two equations of motion separately one obtains a hierarchical structure in terms of an expansion in powers of the interaction parameter, and this permits a systematic solution of the problem. The main disadvantage of the method is that two equations of motion have to be solved, and one has to balance the corresponding powers of the interaction parameter when recombining ϕ_1 and ϕ_2 again to obtain the transition moment M'_{nk}. This can become tedious for the higher-order terms.

As opposed to this, one can give a true density matrix formulation of the problem which requires the solution of only a single equation, viz the Liouville–von Neumann equation. Not only does this simplify the manipulations; it also possesses the added advantage that the effects of radiation damping can be readily incorporated phenomenologically into the treatment. Finally in agreement with earlier work (Stanton 1969), it is to be stressed that the density matrix approach is not only systematic, but also far more compact and simpler to evaluate for the higher-order terms than is the usual approach based on time-dependent perturbation theory.

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