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1975 J. Phys. A: Math. Gen. 8 1313

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## Comments on the formal theory of scattering and relaxation

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Received 17 February 1975

**Abstract.** A tetradic scattering matrix formalism is proposed as a comprehensive framework for describing scattering and relaxation processes of both stationary and non-stationary systems. In the latter case (realized by the scattering of the molecular-maser beam) ordinary dyadic  $T$ -matrix formalism involving on-the-energy-shell scattering amplitudes is inadequate, the introduction of off-the-shell elements being required. Expressions are given relating the tetradic  $\mathcal{T}$ -matrix elements to various scattering and attenuation rates (or cross sections). The relation to the tetradic level-shift operator in relaxation (linear response) theory is discussed. Photon absorption is presented as the successive occurrence of a scattering and a relaxation process, from the point of view of this formalism.

### 1. Introduction

In molecular physics it is customary to distinguish between scattering and relaxation experiments. Although, in dilute samples, both experiments may be related to elementary 'collision' processes, they differ essentially in their preparation and detection modes. In scattering experiments, the scattered particle (or particles) is prepared in some well defined state, usually a stationary state of the Hamiltonian  $H_0$  pertaining to the non-interacting constituents. The products of the scattering process are then analysed in their respective stationary states in terms of the corresponding cross sections. As a matter of principle, such an experiment can be performed with arbitrarily sharp energy resolution. Consequently, the cross sections may be formally related to the  $S$  matrix or, rather, to on-the-energy-shell elements of the scattering ( $T$ ) matrix (cf Goldberger and Watson 1964, Levine 1969).

In relaxation (or decay) experiments, a microscopic subsystem within a material sample is brought into a non-equilibrium state by some external agent (eg, radiation) and its decay back to equilibrium is monitored, with the microsystem in permanent contact with the rest of the sample, acting as a thermal bath (cf Bloch 1946, 1956, 1957, Redfield 1965, Zwanzig 1960a, b, Fano 1963, Abrikosov *et al* 1965, Fetter and Walecka 1971). Formally, such experiments are analysed in terms of retarded Green functions and level-shift operators.

It is well known that the two formal descriptions, that of scattering by the  $T$  matrix and that of relaxation by the level-shift operator, are intimately connected and that, in the low-density limit (binary collision approximation), the latter can be expressed in terms of scattering cross sections (Fano 1963, Ben-Reuven 1975). This close connection is most obvious when the relaxing subsystem is prepared in a well defined stationary

state of its Hamiltonian, and the decay of this state's population is subsequently monitored (a ' $T_1$ ' process) (cf Redfield 1965, Abragam 1961). However, a broad class of relaxation processes (those of the ' $T_2$ ' type) involve an initial preparation in a non-stationary superposition state (eg, by coupling to a molecular moment with off-diagonal elements). Proper description of such processes requires an introduction of tetradic Green functions and level-shift (or line-shift) operators (Fano 1963, Redfield 1965, Ben-Reuven 1975) (or two-time particle-hole Green functions in the terminology of quantum field theory (Abrikosov *et al* 1965, Fetter and Walecka 1971), as opposed to the one-particle Green functions adequate for dealing with  $T_1$  processes). The relation of the tetradic line-shift operator to the  $T$  matrix is much more complicated.

It was recently realized that  $T_2$ -type processes can be studied not only by relaxation but also by scattering experiments (such as the molecular-maser-beam scattering experiment of Kukolich *et al* (1973): see also Wang *et al* (1973)). In such experiments the beam particles are prepared in a non-stationary superposition state and, following their scattering, the beam attenuation in this particular state is measured. It then becomes necessary to extend the introduction of tetradic operators to scattering theory, in order to properly define cross sections and attenuation rates for such ' $T_2$ -scattering' experiments (Ben-Reuven and Kukolich 1973).

The tetradic scattering ( $\mathcal{S}$ ) matrix is introduced below, in analogy to the Lipmann-Schwinger dyadic  $T$  matrix of stationary-state scattering theory (cf Goldberger and Watson 1964). It is then shown how both ( $T_1$  and  $T_2$ ) types of scattering can be analysed in terms of tetradic matrix elements of  $\mathcal{S}$  (Fano 1963, Ben-Reuven 1975). In the stationary ( $T_1$ ) case, elements of  $\mathcal{S}$  directly relate to scattering (or attenuation) rates (or cross sections). In the non-stationary ( $T_2$ ) case, complex rates (the imaginary part corresponding to frequency shifts) are obtained, showing that rates coupling different superposition modes may involve  $T$ -matrix elements lying off the energy shell.

This formalism is exemplified by the analysis of the molecular-maser-beam scattering. Discussion of the connection to relaxation (linear response) theory follows. It is then shown how a single experiment can include both types of processes (ie, scattering and relaxation) as successive events. Such is the case when a particle (eg, a photon) is scattered by a small subsystem (eg, a molecule) which, in turn, is weakly coupled to a thermal bath (eg, collisions with a gas sample and radiative damping). Finally, extensions of the  $T_2$ -type scattering experiments are suggested in the conclusive notes.

## 2. Tetradic scattering matrix

In an ordinary (stationary-state) scattering experiment the reactants are prepared (or products analysed) in terms of eigenstates of the Hamiltonian  $H_0$  of the non-interacting constituents. When our information regarding the state is incomplete, stationary states are characterized by specifying the diagonal elements of a density matrix  $\rho$  in the basis of eigenstates of  $H_0$ . In the non-stationary case the initial preparation state (or final detection state) is specified by a superposition of eigenstates of  $H_0$  (or off-diagonal elements of  $\rho$ ). Such a state can be prepared, for example, by inducing a beam particle in a stationary pure state ( $\psi_a$ ) to go into a superposition state ( $C_a\psi_a + C_b\psi_b$ ) by applying a short radiation pulse of specified duration during which transitions occur between the eigenstates  $a$  and  $b$  of  $H_0$ .

Formal scattering theory provides us with the means for relating the stationary-state wavefunctions  $\psi_a$  (or diagonal density-matrix elements  $\rho_{aa}$ ) at some early time before the

scattering takes place, to other states at a later time after the scattering. In the density matrix language (in the interaction picture), we can write

$$\rho_{cc}(+\infty) = \sum_a S_{ca} \rho_{aa}(-\infty) S_{ac}^\dagger = \sum_a |S_{ca}|^2 \rho_{aa}(-\infty), \quad (1a)$$

where  $S$  is the ordinary  $S$  matrix of the formal theory. Equation (1a) may be rather trivially rewritten in a tetradic matrix fashion

$$\rho_{cc}(+\infty) = \sum_a \mathcal{S}_{cc;aa} \rho_{aa}(-\infty), \quad (1b)$$

where (using a more general definition of Ben-Reuven 1975)

$$\mathcal{S}_{cd;ab} = S_{ca} S_{db}^*. \quad (2)$$

For shorthand, equation (2) will be written  $\mathcal{S} = SS^*$ , with  $S$  operating on the rows of  $\rho$  and  $S^*$  on its columns (the asterisk implying complex conjugation). The  $S$  matrix takes care of energy conservation in equation (1a) since it vanishes unless  $a$  and  $c$  have equal energies, and of probability conservation by its unitarity.

The generalization to non-stationary experiments involving off-diagonal density-matrix elements is not so trivial. One might be tempted to simply apply equation (2), with  $b \neq a$  and  $c \neq d$ , to  $\rho_{ab}(-\infty)$  to obtain  $\rho_{cd}(+\infty)$ . This is, however, not quite the proper thing to do.  $\rho_{ab}$  represents a non-stationary state, and energy conservation arguments should not apply to the scattering process alone (they should include the preparation and detection stages, which involve the use of pulses in a non-adiabatic fashion). Neither are probability conservation arguments relevant to this case.  $\rho_{cd}$  represents, outside the scattering range, an oscillating quantity: its oscillation frequency is measurable over finite time periods, and need not be equal to that of  $\rho_{ab}$ . It is therefore necessary to introduce the more general  $T$  matrix, with possible admission of off-the-energy-shell elements, to the formal description of the long-time behaviour of  $\rho$ . Since the stationary case ( $a = b$ ) is only a special case, and since, anyhow, transition rates (or cross sections) are expressible in terms of the  $T$  matrix, we shall proceed here with a general introduction of the tetradic scattering ( $\mathcal{T}$ ) matrix, and its relation to  $T$ , as a general means of relating  $\rho$  after the scattering to its value before the scattering.

Formally, the introduction of  $\mathcal{T}$  follows from the Liouville-von Neumann equation for the density matrix (cf Fano 1963) in much the same manner as the derivation of the Lippmann-Schwinger  $T$  matrix follows from the Schrödinger equation (cf Goldberger and Watson 1964). The tetradic analogue of the Hamiltonian  $H$  is the Liouvillian  $\mathcal{H}$ , defined as (Fano 1963)

$$\mathcal{H}_{cd;ab} = \hbar^{-1} (H_{ca} \delta_{db} - \delta_{ca} H_{db}^*) \quad (3a)$$

or, in the shorthand notation,

$$\mathcal{H} = \hbar^{-1} (HI^* - IH^*), \quad (3b)$$

$I$  being the identity operator. Let

$$H = H_0 + H_1. \quad (4)$$

where  $H_0$  is the Hamiltonian of the non-interacting incident (or scattered) particles and  $H_1$  is their interaction. (Extension to reactive scattering is rather straightforward and will not be referred to here.) Correspondingly, let

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1. \quad (5)$$

The scattering matrix  $\mathcal{F}$  can be introduced by the tetradic analogue of the Lippmann-Schwinger equation,

$$\mathcal{F}(\omega) = \mathcal{H}_1 + \mathcal{H}_1 \mathcal{G}(\omega) \mathcal{H}_1, \quad (6)$$

where  $\mathcal{G}(\omega)$  is the tetradic retarded Green function for  $\mathcal{H}$ ,

$$\mathcal{G}(\omega) \equiv \lim_{\eta \rightarrow +0} \mathcal{G}(\omega + i\eta) = \lim(\omega - \mathcal{H} + i\eta)^{-1}. \quad (7)$$

The  $\mathcal{F}$  matrix can be expressed in binary forms involving  $T$ -matrix elements defined on the rows of  $\rho$  and  $T^\dagger$ -matrix elements defined on the columns of  $\rho$ . The general expression is (Fano 1963, Ben-Reuven 1975)

$$\begin{aligned} \hbar \mathcal{F}_{cd;ab}(\omega) &= T_{ca}(E_b + \hbar\omega) \delta_{db} - \delta_{ca} T_{db}^*(E_a - \hbar\omega) \\ &+ (2\pi i)^{-1} \int dE \mathcal{D}_{cd;cd} T_{cd}(E + \hbar\omega) T_{db}^*(E) \mathcal{D}_{ab;ab}, \end{aligned} \quad (8)$$

where

$$\begin{aligned} \mathcal{D}_{ab;ab} &= [G_0(E + \hbar\omega) I^* - I G_0^*(E)]_{ab;ab} \\ &= (E + \hbar\omega - E_a + i\eta)^{-1} - (E - E_b - i\eta)^{-1}, \end{aligned} \quad (9)$$

$$G_0(E) = \lim_{\eta \rightarrow +0} (E - H_0 + i\eta)^{-1} \quad (10)$$

being the dyadic retarded Green function for  $H_0$ , and  $E_a, E_b$ , etc, being eigenvalues of  $H_0$ .

Asymptotic behaviour of stationary states is adequately described by on-the-energy-shell elements  $T_{ca}(E)$ , with  $E = E_a = E_c$ , of the scattering matrix. Correspondingly, 'on-the-frequency-shell' elements of  $\mathcal{F}$  are given by (Ben-Reuven 1975)

$$\hbar \mathcal{F}_{cd;ab}(\omega) = T_{ca}(E_a) \delta_{db} - \delta_{ca} T_{db}^*(E_b) + 2\pi i \delta(E_c - E_a) T_{ca}(E_a) T_{db}^*(E_b), \quad (\omega = \omega_{ab} = \omega_{cd}), \quad (11)$$

where  $\omega_{ab} = \hbar^{-1}(E_a - E_b)$ , etc. As is obvious from equation (11), on-the-frequency-shell elements of  $\mathcal{F}$  contain on-the-energy-shell elements of  $T$  and  $T^\dagger$ . Given the dyadic relation between  $S$  and  $T$ ,

$$S_{ca} = \delta_{ca} - 2\pi i \delta(E_c - E_a) T_{ca}(E_a), \quad (12)$$

it follows that

$$\mathcal{S}_{cd;ab} = \delta_{ca} \delta_{db} - 2\pi i \delta(\omega_{cd} - \omega_{ab}) \mathcal{F}_{cd;ab}(\omega_{ab}), \quad (13)$$

where  $\mathcal{S}$  is the tetradic  $S$  matrix of equation (2). Also, on-the-frequency-shell elements of  $\mathcal{F}$  obey the theorem (Fano 1963)

$$i(\mathcal{F}(\omega) - \mathcal{F}^\dagger(\omega)) = 2\pi \mathcal{F}^\dagger(\omega) \delta(\omega - \mathcal{H}_0) \mathcal{F}(\omega), \quad (14)$$

in analogy to the dyadic 'optical' theorem

$$i(T(E) - T^\dagger(E)) = 2\pi T^\dagger(E) \delta(E - H_0) T(E) \quad (15)$$

pertaining to on-the-energy-shell elements of  $T$ .

It is appropriate here to define what is implied by Hermitian conjugation in tetradic notation: ie,

$$(\mathcal{F}^\dagger)_{ab;cd} = \mathcal{F}_{cd;ab}^*. \quad (16)$$

This should be distinguished from another transposition operation, namely Liouvillian conjugation, defined by

$$(\mathcal{T}^\times)_{ab;cd} = \mathcal{T}^*_{ba;dc}. \quad (17)$$

The latter is directly related to Hermitian conjugation of dyadics, as  $(\mathcal{T}X)^\dagger = \mathcal{T}^\times X^\dagger$ ,  $X$  being an arbitrary dyadic. Since  $H$  is Hermitian, and  $S$  is unitary, it follows that

$$\mathcal{H} = \mathcal{H}^\dagger = -\mathcal{H}^\times \quad (18)$$

and

$$\mathcal{S} = (\mathcal{S}^\dagger)^{-1} = \mathcal{S}^\times. \quad (19)$$

Hence  $\mathcal{G}$ , and likewise  $\mathcal{T}$ , obey

$$\mathcal{G}^\dagger(\omega) = \mathcal{G}(\omega^*), \quad \mathcal{G}^\times(\omega) = -\mathcal{G}(-\omega^*), \quad (20)$$

where  $\pm\omega^*$  means replacing  $\omega + i\eta$  by  $\pm(\omega - i\eta)$  in equation (7).

### 3. Level attenuation

We shall now proceed to discuss the meaning of various matrix elements of  $\mathcal{T}$  in terms of scattering rates. We shall classify them, in general, into two classes: elements of the type  $\mathcal{T}_{cc;aa}$  describing  $T_1$ -type processes (level attenuation, or stationary-state scattering), and elements of the type  $\mathcal{T}_{cd;ba}$  ( $a \neq b$ ) describing  $T_2$ -type processes (line attenuation, or non-stationary-state scattering).

Consider the tetradic  $T_1$ -type elements of  $\mathcal{T}$  defined on the zero-frequency shell,

$$\hbar\mathcal{T}_{cc;aa}(0) = (T_{aa}(E_a) - T_{aa}^*(E_a))\delta_{ca} + 2\pi i |T_{ca}(E_a)|^2 \delta(E_c - E_a). \quad (21)$$

Using the optical theorem for  $T$ , equation (15), we can write

$$i\mathcal{T}_{cc;aa}(0) = \Gamma_a \delta_{ca} - \Gamma_{ca}(1 - \delta_{ca}), \quad (22)$$

where

$$\Gamma_{ca} = 2\pi\hbar^{-1} |T_{ca}(E_a)|^2 \delta(E_c - E_a), \quad (23)$$

and

$$\Gamma_a = \sum_{c \neq a} \Gamma_{ca}. \quad (24)$$

Notice that  $a, c$  etc, denote complete sets of quantum numbers (translational and internal) of all participating particles. The summation over  $c$  includes an integration over all continuous quantum numbers. The exclusion of  $c = a$  from the sum in equation (24) implies that the integrals over continuous variables other than energy (eg, scattering angles) should be replaced by Cauchy principal parts.

An off-diagonal element ( $c \neq a$ ) specifies the transition rate ( $\Gamma_{ca}$ ) from state  $a$  to state  $c$ . The diagonal element ( $c = a$ ) specifies the total attenuation rate of level  $a$ . Notice that (unlike the optical theorem for the forward scattering amplitude  $T_{aa}(E_a)$ , which involves the total scattering rate), equation (24) excludes the forward elastic scattering ( $c = a$ ) from the sum. (This is, however, of no practical implication if the scattering amplitude is not singular in the forward direction.) The rates  $\Gamma_{ca}$  are proportional to the flux of incident particles. To introduce flux-independent (and hence

geometry-independent) quantities we can define appropriate cross sections. For example, in the case of one-particle scattering by a heavy target (or two-particle scattering in centre-of-mass coordinates), the cross section for the  $a \rightarrow c$  transition is

$$\sigma_{ca}(E_a) = i\mathcal{F}_{cc;aa}(0)F_a^{-1}, \quad (25)$$

where  $F_a$  is the flux of incident particles in level  $a$ .

In many experiments of this kind it is, however, impossible (or undesirable) to specify the complete set of quantum numbers of all constituents. Suppose only a subsystem (the 'projectile') has fully specified states, whereas the rest (the 'target') can only be specified, at best, by a stationary distribution function. Let  $a, b$ , etc, denote, in this case, the projectile states (including translational degrees of freedom) and  $\alpha, \beta$ , etc, denote target state. Also, let  $\rho_x$ , etc, be the alleged distribution in target states. A reduced tetradic scattering matrix, defined explicitly on projectile states only, is introduced by

$$\langle \mathcal{F}_{cd;ab}(\omega) \rangle = \sum_{x\beta} \mathcal{F}_{c\beta d\beta;axbx}(\omega)\rho_x. \quad (26)$$

It follows from this definition that the reduced level-attenuation rates for the projectile can be derived from

$$i\langle \mathcal{F}_{cc;aa}(0) \rangle = \langle \Gamma_a \rangle \delta_{ca} - \langle \Gamma_{ca} \rangle (1 - \delta_{ca}). \quad (27)$$

Here (for  $c \neq a$ )

$$\langle \Gamma_{ca} \rangle = 2\pi\hbar^{-1} \sum_{x\beta} |T_{c\beta,ax}(E_a + E_x)|^2 \rho_x \delta(E_a + E_x - E_c - E_\beta) \quad (28)$$

is the transition rate from  $a$  to  $c$ , irrespective of changes in the target.

$$\langle \Gamma_a \rangle = \sum_{c \neq a} \langle \Gamma_{ca} \rangle \quad (29)$$

is the total attenuation rate of the projectile beam in state  $a$ , irrespective of target changes. It excludes not only the complete-set forward elastic scattering amplitude ( $a\alpha = c\beta$ ) but also transitions to degenerate target states ( $a\alpha \rightarrow a\beta, \alpha \neq \beta$ ) not affecting the projectile state.

The array of elements defined by equation (27), with rows labelled by  $c$  and columns by  $a$ , is equivalent to the matrix of coefficients in the Pauli master equation (cf eg Van Hove 1955, Prigogine 1962, Zwanzig 1964) for the subsystem (the projectile). Conservation of probability is compatible with

$$i \sum_c \langle \mathcal{F}_{cc;aa}(0) \rangle = 0, \quad (30)$$

where the sum over  $c$  is unrestricted.

#### 4. Line attenuation

Consider now the  $T_2$ -type matrix elements  $\mathcal{F}_{cd;ab}$ , with  $a \neq b$ , pertaining to scattering from a non-stationary state ( $\rho_{ab}$ ). This state represents a resonance mode (or 'spectral line') excitation of the system and therefore the corresponding diagonal tetradic element will be referred to as relating to line attenuation.

The diagonal on-the-frequency-shell elements  $\mathcal{F}_{ab;ab}(\omega_{ab})$  are not pure imaginary, their real part producing a frequency shift of the  $\omega_{ab}$  mode. Applying the optical theorem, equation (15), to equation (11), we obtain

$$-\text{Im } \mathcal{F}_{ab;ab}(\omega_{ab}) = \frac{1}{2}(\Gamma_a + \Gamma_b) + \Gamma_{\text{int}}(ab), \quad (31)$$

where  $\Gamma_a$  is the total attenuation rate of level  $a$ , given by equation (23), etc, and

$$\Gamma_{\text{int}}(ab) = \pi\hbar^{-1} |T_{aa}(E_a) - T_{bb}(E_b)|^2 \delta(E_a - E_b - \hbar\omega_{ab}) \quad (32)$$

is an interference term, involving the difference in forward scattering amplitudes in the two levels ( $a, b$ ) of the resonance mode. The line-attenuation rate thus consists of a ( $T_1$ -type) mean attenuation rate of the two levels, plus the interference term.

Here, again, we can extend the discussion to the case where only the ‘projectile’ is in a well specified state by referring to equation (26). Thus,

$$-\text{Im} \langle \mathcal{F}_{ab;ab}(\omega_{ab}) \rangle = \frac{1}{2}(\langle \Gamma_a \rangle + \langle \Gamma_b \rangle) + \langle \Gamma_{\text{int}}(ab) \rangle, \quad (33)$$

where

$$\langle \Gamma_{\text{int}}(ab) \rangle = \pi\hbar^{-1} \sum_{\alpha\beta} |T_{a\beta, a\alpha}(E_a + E_\alpha) - T_{b\beta, b\alpha}(E_b + E_\alpha)|^2 \rho_\alpha \delta(E_\beta - E_\alpha) \quad (34)$$

involves interference of scattering amplitudes diagonal in projectile states.

The non-stationary mode ( $ab$ ) may be coupled to another mode ( $cd$ ). For example, we can prepare the projectile by excitation with a pulse in resonance with the  $a \rightarrow b$  transition and monitor the scattered beam by a pulse in resonance with the  $c \rightarrow d$  transition. The (complex) rate for such coupling is given by  $\mathcal{F}_{cd;ab}$  (or by  $\langle \mathcal{F}_{cd;ab} \rangle$  in the reduced case). However, the two mode frequencies,  $\omega_{ab}$  and  $\omega_{cd}$ , need not necessarily be equal, and therefore the rates can not be related to elements of  $\mathcal{F}$  (or  $T$ ) strictly confined to the frequency (energy) shell. The relation of  $\rho(+\infty)$  to  $\rho(-\infty)$  is no more describable by a Markoffian-type rate equation, but by an integro-differential equation of the generalized Langevin type (cf Zwanzig 1960a, b, Mori 1965a, b), with a memory kernel. A differential rate equation form can be nevertheless retained under certain *approximate* conditions. Suppose all ‘upper’ states ( $a, c$ , etc) and all ‘lower’ states ( $b, d$ , etc) of the various resonance modes concerned lie each within a narrow band of energies  $\Delta E$  over which  $T_{aa}(E + \hbar\omega)$  and  $T_{bb}(E)$ , etc, do not vary appreciably with  $E$ . Ordinarily, if there is no long-lived resonance (or quasi-bound) state of the colliding particles, there exists such an interval; it may serve to define a ‘collision’ time

$$\tau_c \simeq \hbar/\Delta E \quad (35)$$

(typically of the order of a picosecond for molecular collisions at thermal energies), which is a slowly varying function of  $E$ . We may then replace the variable argument of  $\mathcal{F}_{ab;cd}(\omega)$  by some fixed value  $\bar{\omega}$  lying within the band of resonance frequencies  $\omega_{ab}$ , etc. By ‘coarse graining’ over time intervals large compared to  $\tau_c$ , a differential rate equation similar in form to the Bloch–Redfield equation may be written,

$$(\partial/\partial t)\langle \rho \rangle = -i(\Omega + \langle \mathcal{F}(\bar{\omega}) \rangle)\langle \rho \rangle, \quad (36)$$

where  $\langle \rho \rangle$  is the subsystem (projectile) reduced density matrix, defined on the band of modes  $ab$ , etc, confined by  $\Delta E$ . Here

$$\Omega_{cd;ab} = \omega_{ab} \delta_{ca} \delta_{db} \quad (37)$$

is the (diagonal) tetradic of resonance frequencies. The similarity to the Bloch–Redfield



rate equation is in form only: the rate coefficients may be different, as we shall see later on, dealing with relaxation experiments.

Equation (36) does not strictly confine the  $\mathcal{T}$  matrix to on-the-energy-shell elements of  $T$  and  $T^\dagger$  (though it may be *approximately* expressed by such). We should thus admit that energy conservation arguments, strictly enforcible in ( $T_1$ -type) scattering of stationary states, do not apply here. As already stated above, energy conservation arguments should rather apply to the whole sequence of preparation–scattering–detection events, in which the non-adiabatic application of pulses is involved. The mode  $cd$ , represented by  $\rho_{cd}$ , oscillates through the time-dependent factor  $\exp(-i\omega_{cd}t)$ . The oscillation frequency is measurable (ie, it requires monitoring  $\rho_{cd}$  over a finite period of time and not just its asymptotic value), and therefore need not be equal to that of the initial mode ( $ab$ ).

## 5. The maser beam

Maser-beam scattering (Kukolich *et al* 1973) provides an example of a scattering experiment in which the projectile can be prepared in either a stationary or a non-stationary superposition state. Ammonia molecules, for example, can be selected in one of the two parity states of the inversion doublets, and then brought to a superposition state by application of a  $\pi/2$  pulse of microwave radiation. The monitoring of the attenuated beam, after passing through a scattering chamber, is then made possible by applying a similar pulse, phase-matched to the previous one.

The ideal two-level maser consists of only two internal states ( $a$  and  $b$ ), which may be coupled by a radiative transition. The tetradic  $\mathcal{T}$  matrix has thus four available ‘channels’  $aa$ ,  $bb$ ,  $ab$ , and  $ba$ . In the terminology of Liouville-space (or double-space) vectors (Fano 1963) on which tetradic operators are defined, the four channels span, respectively, four orthogonal subspaces, in each of which vectors are labelled by translational and target degrees of freedom (or by translational alone, in the target-reduced  $\langle \mathcal{T} \rangle$  formalism).

Consider the relevant forward scattering amplitudes in the various channels. Let  $p, q$ , etc, denote translational states (with  $p$  reserved for the incoming beam). In the  $aa$  channel,

$$i\langle \mathcal{T}_{apap;apap}(0) \rangle = \Gamma_a = \Gamma_{el}(a) + \Gamma_{ba}. \quad (38)$$

Here (dropping further explicit reference to the target-reducing angular brackets),

$$\Gamma_{el}(a) = \sum_{\alpha\beta} \sum_{q \neq p} |T_{a\beta q, a\alpha p}(E_{a\alpha p})|^2 \rho_x \delta(E_{a\beta q} - E_{a\alpha p}) \quad (39)$$

is the total elastic scattering rate of maser molecules in state  $a$  (in non-forward directions), and

$$\begin{aligned} \Gamma_{ba} &= -i\langle \mathcal{T}_{bpbp;apap}(0) \rangle \\ &= \sum_{\alpha\beta} \sum_q |T_{b\beta q, a\alpha p}(E_{a\alpha p})|^2 \rho_x \delta(E_{b\beta q} - E_{a\alpha p}) \end{aligned} \quad (40)$$

is the rate of inelastic ( $a \rightarrow b$ ) transitions. Equation (40) also provides the coupling of the  $aa$  to the  $bb$  channels.

The attenuation of the  $ab$  mode is related to the  $T_2$ -type element of  $\mathcal{T}$ ,

$$i\langle \mathcal{T}_{apbp;apbp}(\omega_{ab}) \rangle = \frac{1}{2}(\Gamma_a + \Gamma_b) + \tilde{\Gamma}_{inl}(ab) \quad (41)$$

(the tilde denoting a complex 'rate'). A similar result is obtained for the  $ba$  mode, with the complex interference term  $\tilde{\Gamma}_{\text{int}}(ba) = \tilde{\Gamma}_{\text{int}}^*(ab)$ . The  $ab$  channel is coupled to the  $ba$  channel by the complex rate

$$-i\langle \mathcal{T}_{bpa; a\bar{p}b}(0) \rangle \equiv \tilde{\Gamma}_{\text{ex}}(ba; ab) = \tilde{\Gamma}_{\text{ex}}^*(ab; ba), \quad (42)$$

with  $\text{Re}(\tilde{\Gamma}_{\text{ex}})$  representing a mixing (or exchange) rate of the resonant ( $ab$ ) and anti-resonant ( $ba$ ) modes (Ben-Reuven 1966, 1969). Here we have taken  $\bar{\omega} = 0$  for the 'band' of close-lying modes  $ab$  and  $ba$  (assuming  $2|E_a - E_b|$  is within the interval  $\Delta E \simeq \hbar\tau_c^{-1}$ ).

General expressions for  $\tilde{\Gamma}_{\text{int}}$  and  $\tilde{\Gamma}_{\text{ex}}$  follow directly from the definition of  $\mathcal{T}$  and will not be given here explicitly. However, they can be much simplified under certain approximate conditions (Ben-Reuven and Kukolich 1973). In many instances (such as, eg, the ammonia maser at thermal energies), the scattering amplitudes are practically insensitive to the interchange of  $a$  with  $b$ , implying equal behaviour of the two levels in the scattering process. We may then write (assuming the interaction matrix  $V_{ab}$  is real)

$$T_{aa} \simeq T_{bb}, \quad T_{ab} \simeq T_{ba}, \quad (43)$$

etc, for the  $T$  matrix in the two maser levels. Under such circumstances,

$$\tilde{\Gamma}_{\text{int}} \simeq 0, \quad (44)$$

and

$$\tilde{\Gamma}_{\text{ex}} \simeq \Gamma_{ba} \simeq \Gamma_{ab}, \quad (45)$$

equal to the inelastic scattering rate (equation (40)).

Cross coupling between  $T_1$ -type ( $aa$ ) and  $T_2$ -type ( $ab$ ) channels is in many cases excluded by symmetry arguments (eg, inversion symmetry in ammonia). We therefore have, under the approximations made above, altogether two distinct rates: the elastic attenuation rate  $\Gamma_{e1}$  and the inelastic scattering rate  $\Gamma_{ba}$ . The tetradic  $\langle \mathcal{T} \rangle$  operator, considered as a  $4 \times 4$  supermatrix in the four channel labels, can be diagonalized (under the preceding simplifications) by introducing the Feynman–Vernon–Hellwarth (Feynman *et al* 1957) representation.

Let the double-bracket symbol  $|ab\rangle\rangle$  (cf Baranger 1958, Ben-Reuven 1975) represent the double-space (Liouville-space) vectors corresponding to the  $ab$  mode on which  $\mathcal{T}$  is defined, etc. The four channels under which  $\mathcal{T}$  reduces to the diagonal form are

$$\begin{aligned} |0\rangle\rangle &= 2^{-1/2}(|aa\rangle\rangle + |bb\rangle\rangle), \\ |1\rangle\rangle &= 2^{-1/2}(|ab\rangle\rangle + |ba\rangle\rangle), \\ |2\rangle\rangle &= i2^{-1/2}(|ab\rangle\rangle - |ba\rangle\rangle), \\ |3\rangle\rangle &= 2^{-1/2}(|aa\rangle\rangle - |bb\rangle\rangle). \end{aligned} \quad (46)$$

In these four channels (dropping explicit reference to the translational state label  $p$ )

$$\begin{aligned} i\langle \mathcal{T}_{0;0} \rangle &= i\langle \mathcal{T}_{1;1} \rangle = \Gamma_{e1}, \\ i\langle \mathcal{T}_{2;2} \rangle &= i\langle \mathcal{T}_{3;3} \rangle = \Gamma_{e1} + 2\Gamma_{ba}. \end{aligned} \quad (47)$$

Channel 0 represents the total population of the beam, irrespective of the internal ( $a$  or  $b$ ) states, and is affected only by the total attenuation rate (in non-forward directions) of the beam, irrespective of internal-state changes. The other three modes constitute the Feynman–Vernon–Hellwarth analogue of the Bloch 'vector' for optical (or microwave) transitions. The three 'components' of this 'vector' are unequally attenuated. Notice,

however, that, this unequal behaviour does not follow the traditional division into  $T_1$  and  $T_2$  rates in Bloch's equation, but it rather follows from the uneven effect of the inelastic scattering rate.

The representation introduced by equation (46) can be transformed to a 'rotating frame' (cf Abragam 1961), rotating the 1 and 2 components with an angular velocity  $\omega \simeq \omega_{ab}$ . Neglecting rapidly oscillating terms ('rotating frame' approximation),  $\mathcal{T}_{1;1}$  and  $\mathcal{T}_{2;2}$  are mixed so that, in the new (rotating) frame,

$$i\langle \mathcal{T}_{1;1}^{(r)} \rangle = i\langle \mathcal{T}_{2;2}^{(r)} \rangle = \Gamma_{e1} + \Gamma_{ba}. \quad (48)$$

Notice, however, that (contrary to the prevailing usage with regard to Bloch's equation) this rate is *smaller* than  $i\langle \mathcal{T}_{3;3} \rangle$  by an amount equal to the inelastic scattering rate ( $\Gamma_{ba}$ ).

## 6. Relaxation experiments

We have seen how the tetradic matrix provides a formal framework for the general discussion of scattering experiments, both of the  $T_1$  type, with the beam prepared in a stationary state, and of the  $T_2$  type, with the beam prepared in a non-stationary superposition state.

Consider a subsystem of type A (eg, a molecule) in continuous contact with a large system in thermal equilibrium, consisting of other subsystems, of type B. Let us assume that the coupling of A to the thermal bath B is sufficiently weak, and long-time statistical correlations can be neglected (Fano 1963). Suppose now that A is prepared by a sudden excitation (eg, by a radiation pulse) in some non-equilibrium state, eg, a well defined stationary state of its Hamiltonian  $H_A$ , or a non-stationary (superposition) state. The time evolution of A is then monitored by an appropriate means (eg absorption or fluorescence for stationary states, or pulse techniques for non-stationary states).

Let

$$H = H_A + H_B + H_1 \quad (49)$$

be the Hamiltonian of A and the bath B interacting through  $H_1$ . The corresponding Liouvillian

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_1. \quad (50)$$

Neglecting initial correlations between A and B at the moment of excitation of A, we may write

$$\rho(0) = \rho_A(0)\rho_B, \quad (51)$$

where  $\rho_A(0)$  is specified by the mode of excitation, while  $\rho_B$  is a canonical distribution, representing a thermal equilibrium. Since we monitor A alone, we are interested only in the reduced density matrix for A, obtained by taking the trace over all B degrees of freedom,

$$\rho_A(t) = \text{Tr}_B \rho(t) = \text{Tr}_B [\exp(-i\mathcal{H}t)\rho_A\rho_B]. \quad (52)$$

Applying to  $\rho(t)$  the projection operators, defined by Zwanzig (1960a, b) (see also Fano 1963)

$$\hat{P}X = \rho_B \text{Tr}_B(X), \quad \hat{Q} = 1 - \hat{P}, \quad (53)$$

it follows that

$$\rho_A(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} \exp(-i\omega t) \langle \mathcal{G}(\omega) \rangle \rho_A(0). \quad (54)$$

Here, following Zwanzig's (1960a, b) method

$$\langle \mathcal{G}(\omega) \rangle = (\omega - \mathcal{H}_A - \langle \mathcal{R}(\omega) \rangle)^{-1} \quad (55)$$

is the reduced tetradic retarded Green function for A. It is expressed in terms of the proper tetradic self-energy (or line-shift) operator

$$\langle \mathcal{R}(\omega) \rangle = \text{Tr}_B(\mathcal{R}(\omega)\rho_B), \quad (56)$$

where

$$\mathcal{R}(\omega) = \mathcal{H}_1 + \mathcal{H}_1 \hat{Q}(\omega - \hat{Q} \mathcal{H} \hat{Q} + i\eta)^{-1} \hat{Q} \mathcal{H}_1. \quad (57)$$

Notice that the brackets here, implying a trace over the bath, have a role similar to that of the brackets over  $\mathcal{T}$  in previous sections with respect to the reduction of target degrees of freedom.  $\mathcal{R}$  is, however, different from  $\mathcal{T}$  owing to the intermediary disposition of the operators  $\hat{Q}$  in equation (57), unlike equation (6).

A rate equation, similar to equation (36), can be obtained, with  $\langle \mathcal{R} \rangle$  replacing  $\langle \mathcal{T} \rangle$ , by making similar approximations. Suppose one may define a correlation time  $\tau_c$  for the interaction with the bath, as a collision time was defined for the scattering by the target. It is then possible to neglect the variation of  $\langle \mathcal{R}(\omega) \rangle$  with  $\omega$  over a range

$$\Delta\omega \ll \tau_c^{-1}, \quad (58)$$

and write

$$(\partial/\partial t)\rho_A = -i(\mathcal{H}_A + \langle \mathcal{R}(\bar{\omega}) \rangle)\rho_A \quad (59)$$

for the element  $\rho_{ab}$ , etc, of  $\rho_A$ , with values of  $\omega_{ab}$  lying within the range  $\Delta\omega$  around  $\bar{\omega}$ . The ensuing Bloch-Redfield rate equation for relaxation differs from the one for scattering, equation (36), insofar as  $\langle \mathcal{R} \rangle$  differs from  $\langle \mathcal{T} \rangle$ . Here, the Hermitian part of  $\langle \mathcal{R} \rangle$  produces frequency shifts, and its anti-Hermitian part plays the role of a relaxation matrix, in the manner that the anti-Hermitian part of  $\langle \mathcal{T} \rangle$  describes the various scattering rates.

The two operators  $\mathcal{T}$  and  $\mathcal{R}$  are related by the integral equation (Fano 1963)

$$\mathcal{T} = \mathcal{R} + \mathcal{R} \hat{P} \mathcal{G}_A(\omega) \hat{P} \mathcal{R}, \quad (60)$$

where

$$\mathcal{G}_A(\omega) = (\omega - \mathcal{H}_A + i\eta)^{-1} \quad (61)$$

is the retarded Green function for the free subsystem A.  $\mathcal{T}$  is related to  $\mathcal{R}$  as the self-energy to the proper self-energy in quantum field theory. Whenever the bath is a dilute gas, the projection operator  $\hat{P}$  introduces (through the summation over B states) the number density of bath molecules  $n_B$  as a factor (cf Ben-Reuven 1975). The expansion of  $\mathcal{T}$  in equation (60) in powers of  $\mathcal{R}$  therefore amounts to an expansion in powers of the density (Albers and Oppenheim 1972). To lowest order in  $n_B$  (the binary collision approximation),  $\langle \mathcal{R} \rangle$  and  $\langle \mathcal{T} \rangle$  are interchangeable, and one may then indiscriminately talk about scattering and relaxation rates.

## 7. Photon absorption

Consider the absorption of a monochromatic beam of photons by a molecule weakly coupled to a thermal bath. This will provide an example of a case in which scattering and relaxation occur as successive events.

The Hamiltonian for this problem is

$$H = H_A + H_B + H_1 + H_R + V = H_M + H_R + V, \quad (62)$$

where  $H_M$  is the Hamiltonian for the molecule-plus-bath system, as defined by equation (49),  $H_R$  is the Hamiltonian of the radiation field and  $V$  is the molecule-radiation interaction. The bath, it is assumed, does not interact with the field.

The radiation field has many modes with which the molecule can interact and photons can be emitted and re-absorbed by the molecule, creating the so called vacuum fluctuations (or radiation noise; cf Heitler 1954). As a result, the mean number of photons in each mode will fluctuate. However, given sufficiently high temperatures and strong beam intensities these fluctuations will be very small in comparison to the number of photons in the incident beam. These fluctuations produce radiative damping of the molecular levels, and we should present them as part of the relaxation process, rather than the scattering (Cohen-Tannoudji 1968, Haroche 1971). It is therefore necessary to redistribute the various terms in the Hamiltonian, sorting out those parts of  $H_R$  and  $V$  representing the particular beam mode and its interaction with the molecular system.

Let the beam mode be denoted by  $k$ . Writing

$$H_R = H_k + H'_R = H_k + \sum_{j \neq k} H_j, \quad (63)$$

and similarly

$$V = V_k + V' = V_k + \sum_{j \neq k} V_j, \quad (64)$$

we can add equations (63) and (64) to  $H_B$  and  $H_1$ , respectively, as a part of the thermal bath. Let the initial states of the molecular Hamiltonian  $H_A$  be labelled  $a, b$ , etc. The initial beam state (in the occupation-number representation) is  $n_k$ . Normalizing the field modes in a box of dimension  $L$ , we may write

$$V_k |a, n_k\rangle = \sum_b L^{-3/2} [v_{ba}(\mathbf{k}) n_k^{1/2} |b, n_k - 1\rangle + v_{ba}(-\mathbf{k}) (n_k + 1)^{1/2} |b, n_k + 1\rangle], \quad (65)$$

where  $\mathbf{k}$  is the wavevector of the beam, and  $v(\mathbf{k})$  is an operator defined on the degrees of freedom of A. In the electric dipole approximation,

$$v(\mathbf{k}) = (\frac{1}{2} \hbar c |\mathbf{k}|) \boldsymbol{\mu}_A \cdot \boldsymbol{\epsilon} \exp(i\mathbf{k} \cdot \mathbf{r}_A), \quad (66)$$

where  $\boldsymbol{\epsilon}$ ,  $\boldsymbol{\mu}_A$  and  $\mathbf{r}_A$  are, respectively, the polarization of the beam, the dipole moment and position of molecule A. The two parts of equation (65) represent, respectively, absorption and emission of a photon. The unity in  $(n_k + 1)^{1/2}$  represents spontaneous emission. It will add up a small contribution to the radiation noise, negligible in comparison to the induced effect as  $n_k \gg 1$ . We shall therefore approximate  $(n_k + 1)^{1/2}$  by  $n_k^{1/2}$  in equation (65).

Given a beam flux

$$F_k = cL^{-3} n_k, \quad (67)$$

the total attenuation cross section of the beam (irrespective of changes in the molecular states, which are characterized by the initial distribution  $\rho$ ) is

$$\sigma_k = i \left\langle \sum_{ac} \mathcal{F}_{cn_k cn_k; an_k an_k}(0) \rho_a \right\rangle F_k^{-1}. \tag{68}$$

Considering  $V_k$  to lowest order only (the first Born approximation), we may write

$$\mathcal{F}(0) \simeq \mathcal{V}_k \mathcal{G}_k(0) \mathcal{V}_k, \tag{69}$$

where  $\mathcal{V}_k$  is the tetradic Liouvillian corresponding to  $V_k$ , and

$$\mathcal{G}_k(\omega) = (\omega - \mathcal{H}' - \mathcal{H}_k + i\eta)^{-1}. \tag{70}$$

Here  $\mathcal{H}'$  is the Liouvillian corresponding to

$$H' = H - H_k - V_k, \tag{71}$$

the Hamiltonian of the molecule A interacting with the generalized bath (including the radiation noise as well as the molecular bath) in the absence of the beam.

Since

$$(\mathcal{H}_k)_{n_k \pm 1, n_k; n_k \pm 1, n_k} = \pm \omega_k, \tag{72}$$

where  $\hbar\omega_k$  is the beam-photon energy, we can replace  $\mathcal{G}_k(0)$  by  $\mathcal{G}(\omega_k)$ , with  $\mathcal{G}$  depending on  $\mathcal{H}'$  only, for the induced emission part of  $V_k$ , and by  $\mathcal{G}(-\omega_k^*) = -\mathcal{G}^*(\omega_k)$  for the induced absorption part, thus removing further explicit reference to the beam degrees of freedom. Keeping all this in mind, considering the definition of Liouvillian conjugation, equation (16), and noting that the elements in equation (68) are pure imaginary, we end up with

$$\sigma_k = -(c\hbar^2)^{-1} 2 \operatorname{Im} \sum_{abcd} v_{ac}^*(\mathbf{k}) v_{ba}(\mathbf{k}) (\rho_a - \rho_b) \langle \mathcal{G}_{ac;ba}(\omega_k) \rangle. \tag{73}$$

So, the scattering cross section for attenuation (absorption) of the beam is expressible in terms of a reduced tetradic retarded Green function of the molecule which, in turn, is coupled to the thermal (molecular and radiative) bath through the  $\langle \mathcal{H} \rangle$  tetradic of relaxation theory (equation (56)).

In the foregoing discussion we have dealt with molecule A and the bath as statistically uncorrelated, ie,

$$\rho = \rho_A \times \rho_B \tag{74}$$

(with  $\rho_B$  representing an equilibrium distribution). Equation (73) is readily modified to include such correlations by not discriminating between the two, writing

$$\sigma_k = -(c\hbar^2)^{-1} 2 \operatorname{Im} \operatorname{Tr}(v^\dagger(\mathbf{k}) \mathcal{G}(\omega_k) [v(\mathbf{k}), \rho]), \tag{75}$$

where  $\rho$  is a combined molecule-plus-bath equilibrium distribution. The Zwanzig projection operators should be redefined to include the effect of the statistical correlations (cf Ben-Reuven 1975) or the trace in equation (75) be calculated by other means. For example, whenever  $\rho$  is a grand canonical distribution, the method of finite-temperature (imaginary-time) Green functions of quantum field theory can be applied (Abrikosov *et al* 1965, Fetter and Walecka 1971, Ross 1966, Bezzerides 1969a, b).

## 8. Conclusions

We have presented above a tetradic scattering matrix formalism as a combined framework for discussing both scattering and relaxation experiments where the initial and the final states are either stationary ( $\rho_{aa}$ ) or non-stationary ( $\rho_{ab}$ ).

The following conclusions were reached.

(i) Scattering from stationary states ( $T_1$ -type) is completely specified by on-the-energy-shell elements of the  $T$  matrix, whereas scattering from non-stationary states may require also off-the-energy-shell elements. In the former (stationary) kind of scattering, the tetradic  $\mathcal{T}$ -matrix formalism is a rather trivial variant of the ordinary  $T$ -matrix formalism. This is not so in the latter (non-stationary) case, where the ordinary (dyadic) scattering formalism is inadequate. We should notice, however, that even in the stationary-state case the tetradic formalism brings forward some features latent in the ordinary formalism (such as the relation of the  $\mathcal{T}_{bb,aa}$  elements to the rate coefficients of the Pauli master equation).

(ii) Relaxation rates can be expressed in terms of a tetradic level-shift operator  $\mathcal{R}$  which, in the low-density limit, is indistinguishable from  $\mathcal{T}$ . Conclusions concerning  $\mathcal{T}$  are equally attributable to  $\mathcal{R}$  in this limit. Elements  $\mathcal{T}_{cd,ab}$  connecting the two non-stationary modes  $ab$  and  $cd$  are, for example, intimately related to cross relaxation between spectral lines associated with the two modes (cf Baranger 1958).

(iii) Experiments can be performed in which scattering and relaxation occur as successive steps in a hierarchy of elementary processes (eg, the absorption of radiation by a molecule coupled to a thermal bath).

(iv) A reduced  $\mathcal{T}$ -matrix formalism is introduced to handle situations where the state of the scattered particles is not specified completely (eg, when the state of the 'projectile' is well specified, whereas that of the 'target' is only describable by some statistical distribution). This reduction procedure is formally similar to the 'bath averaging' in relaxation theory.

A full scope of the problems to which the tetradic formalism applies thus emerges. It includes ordinary (stationary-state) scattering, with target state fully or partially specified, as well as non-stationary state (maser-beam) scattering. In addition, it covers relaxation processes of the  $T_1$  type (level decay) and the  $T_2$  type (line attenuation).

The formalism described above should suggest new kinds of experiments. For example, maser-beam experiments performed so far involved only attenuation (forward scattering) measurements. It should be possible, in principle, to perform experiments in which the scattered beam is monitored in a non-forward direction, or in a non-stationary resonance mode different from the one in which it was originally prepared.

## Acknowledgments

The authors wish to thank Professors S Alexander, J Jortner, and R D Levine, for illuminating discussions.

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