COLLISIONAL BROADENING OF SPECTRAL LINE SHAPE IN TWO-PHOTON AND MULTIPHOTON PROCESSES

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Abstract:
The dressed atom picture and the tetradic \( \mathcal{F} \) matrix are used to develop a unified theoretical framework for the microscopic description of collisional broadening in multiphoton processes. We consider ordinary absorption (single photon processes), two photon processes (absorption and Raman spectra) and saturation effects in multiphoton processes (absorption and Raman spectra in a strong radiation field). Various approximation schemes such as the cluster and the perturbative expansion, semiclassical and stochastic methods and the static and the impact limits are discussed. Special attention is given to the factorization approximation which appears in the present formalism in a natural way, and allows us to use the enormous progress made in the studies of single photon line shapes to construct useful approximations for multiphoton processes. The inclusion of nonimpact phenomena is therefore straightforward within the present approach. Some numerical calculations are presented to demonstrate the applicability of the methods developed in this article.
1. Introduction

Studies of nonlinear optical phenomena such as two-photon absorption, Raman and fluorescence spectra, multiphoton absorption and ionization of atoms and molecules, four wave mixing, etc. have drawn considerable attention to recent years, by virtue of the enormous advances in experimental techniques and resolution [1—9]. The common theoretical model which applies to these problems consists of a few-level system (the "absorber") which interacts with an electromagnetic field and with an external bath consisting of many degrees of freedom. The bath usually causes relaxation and the absorber–bath interaction influences significantly the time evolution of the absorber. The conventional theoretical tool in these studies which was applied with a remarkable success for numerous different experimental situations is the multilevel Bloch equations [10—12]. In these equations the radiation field is treated classically and the effects of the bath are incorporated by the addition of phenomenological level relaxation ($T_1$) and dephasing ($T_2$) rates into the Liouville equation for the isolated absorber plus field. The classical treatment of the radiation field is justified in many cases [13—15] and is usually equivalent to the fully quantum mechanical "dressed atom" approach [16—18] with the exception of phenomena such as spontaneous emission. The phenomenological treatment of relaxation pauses several serious fundamental problems. A direct consequence of this treatment is that an ordinary line shape is predicted to have a simple Lorentzian form (eq. (131b)). Moreover, all few-photon and multiphoton cross sections are given as sums of products of Lorentzian complex amplitudes (eq. (131)). This simplicity which provides a very convenient way for back of the envelope interpretation of experiments, is obviously at the expense of rigor, and is often in disagreement with experimental facts. A few examples are:

(1) It is well established both experimentally and theoretically that no ordinary line shape is Lorentzian in its far wings, which means that even if the simple Bloch equations hold for small detunings they will fail in the wings [19, 20]. The detailed study and analysis of spectral line shapes in the wings may therefore yield microscopic information regarding the dynamical interactions in the system, provided an adequate theory is available.

(2) Precise measurements of spectral line shapes near the line center show asymmetries which are in contradiction to the simple Lorentzian form, even in cases where the latter is most likely to hold [21, 22].

(3) Single photon line shapes are often adequately evaluated in the static limit where the deviations from a Lorentzian behavior are very significant [19, 20].

(4) In multiphoton processes there are pressure induced effects such as the collisional redistribution in resonance Raman [23, 24] and two photon absorption [25] or collisional induced resonances in four wave mixing [26, 27] (the so-called PIER 4 or its solid state analogue DICE signals). In these cases the magnitude of the effect itself (and not just its behavior in the wings) depends on the behavior in the wings of some line shapes. As a result these effects provide a convenient and sensitive way to study line shapes at large detunings [28] where the Lorentzian form fails. For resonance Raman in a three level system there is a coherent and an incoherent (redistribution) component of the scattered radiation. The theoretical treatment based on the Bloch equations [29] predicts that the ratio of these two components is independent on the detuning of the exciting radiation. This is in marked contrast with reality, since the redistribution component actually vanishes much faster than the coherent component as the detuning is increased [24] (see section 5).

The problem of ordinary (single photon) absorption line shapes has been treated in the literature by numerous methods (cluster expansion, perturbation theory, semiclassical methods, stochastic ap-
proaches, etc.) and is well understood [30–43]. By now, there exists the unified theory of spectral line shapes which enables us to calculate microscopically collisionally broadened line shapes, using the potentials of interaction. The purpose of the present article is to develop and apply a simple and unified microscopic description of two photon and multiphoton processes in the presence of a thermal bath without relying on the Bloch’s equations. The basic tool in the present formulation is the tetradic scattering formalism [34, 38, 39], which together with the dressed atom picture enables us to write very conveniently closed formal expressions for the experimental observables. This is a natural starting point for various approximations which finally yield a convenient scheme for the microscopic interpretation of experimental data. In particular, we develop the factorization approximation which enables us to write the cross section for any multiphoton process as a product of single photon complex line shape functions. We can then make use of the enormous progress made in the theoretical treatment of the latter quantities.

This review is divided into four major parts. Part A (sections 1–3) is devoted to introducing the Hamiltonian and the general tetradic $T$ matrix and the dressed atom formulation. In part B (sections 4 and 5) we apply the general formulation to weak field line shapes (single photon absorption and two photon processes) and in part C (sections 6, 7) we apply it to strong field phenomena (multiphoton processes), i.e. absorption and Raman spectra in the presence of a strong radiation field. Finally part D contains some concluding remarks. Although the present review focusses on collisional broadening, many of the formal results apply to more general types of baths (phonons [44–49], intramolecular broadening [50–53], etc.). The present review is not intended to provide a comprehensive survey of the literature and is basically a summary of recent progress in the field. The references given here were chosen for the convenience of the readers and in many cases we cite recent review articles rather than the original contributions.

2. The model Hamiltonian

In this section we shall introduce the basic model Hamiltonian which will be used throughout the present article. We consider a fluid with $N + 1$ atoms contained in a volume $\Omega$. We assume that one atom, denoted $s$ (the absorber), has a few internal states $|{\tilde{\nu}}\rangle = |\tilde{a}\rangle, |\tilde{b}\rangle, |\tilde{c}\rangle...$ and interacts with an external radiation field whereas the other $N$ atoms are structureless bath perturbers which interact with $s$ and with each other. This model allows us to treat foreign broadening. When the perturbers and the absorber are identical particles we have self broadening. Many of the results presented here apply to self broadening as well, provided the rate of resonant exchange of excitation is sufficiently slow. The total Hamiltonian $H$ of the absorber plus bath plus the radiation field will be written as

$$H = H_M + H_R + V.$$  \hspace{1cm} (1) 

Here $H_M$ is the matter Hamiltonian, $H_R$ is the Hamiltonian of the free radiation field and $V$ is the radiation-matter interaction,

$$H_M = \sum_{\tilde{\nu}} \langle \tilde{\nu} | \left( H_{\nu} + \varepsilon_{\nu} - \frac{i}{2} \gamma_{\nu} \right) | \tilde{\nu} \rangle, \quad \tilde{\nu} = \tilde{a}, \tilde{b}, \tilde{c},...$$  \hspace{1cm} (1a) 

$$H_R = \sum_{k} \omega_k a_k^\dagger a_k,$$  \hspace{1cm} (1b)
and
\[ V = \sum_k \sum_{\nu \nu'} \mu_{\nu \nu'}(a_k^\dagger + a_k) |\nu\rangle \langle \nu'|. \] (1c)

\( \nu \) runs over the internal states of the absorber and \( \epsilon_\nu \) and \( \gamma_\nu \) are the energy and the inverse lifetime of an isolated absorber in the \(|\nu\rangle\) state. \( H_R \) is given by the sum over all modes \( k \) of the radiation field with frequency \( \omega_k = kc \). \( a_k^\dagger \) and \( a_k \) are the usual creation and annihilation operators of the field. \( \mu_{\nu \nu'} \) is the transition moment between the \( \nu \) and \( \nu' \) states of the absorber [13]

\[ \mu_{\nu \nu'} = \frac{\epsilon}{m} \sqrt{\frac{2\pi \hbar}{\omega_k \Omega}} \langle \nu | P | \nu' \rangle \] (2)
e, \( m \) and \( P \) being the electronic charge, mass and the momentum operator, respectively. \( \Omega \) is the volume of the system.

The Hamiltonian \( H_\nu \) will be taken in the form:

\[ H_\nu = H_0 + \sum_{p=1}^N U^{\nu p}(Q_\nu - Q_p) + \sum_{p,p'=1}^N U^{\nu \nu'}(Q_p - Q_{p'}) \] (3)

where

\[ H_0 = T_s + \sum_{p=1}^N T_p. \] (4)

Here \( H_0 \) is the kinetic energy operator for the absorber \( (T_s) \) and the perturbers \( (T_p) \), \( U^{\nu p} \) is the adiabatic interaction potential of the absorber in the \( \nu \) state and a perturber, located at \( Q_\nu \) and \( Q_p \) respectively, whereas \( U^{\nu \nu'} \) is the inter-perturber interaction. We have assumed pairwise additive interactions between all particles and we neglect non-adiabatic terms. For the subsequent manipulations we shall introduce a few more quantities. We define a system (absorber plus radiation) Hamiltonian \( H_s \), and decompose it into \( \tilde{H}_s \) and \( H_1 \) in the following way:

\[ H_s = H_M + H_R = H_1 + \tilde{H}_s \] (5)
\[ \tilde{H}_s = \sum_\nu |\nu\rangle \left( \epsilon_\nu - \frac{1}{2} \gamma_\nu \right) \langle \nu| \] (5a)
\[ H_1 = \sum_\nu |\nu\rangle H_\nu \langle \nu| + H_R. \] (5b)

The combined state of the absorber plus bath plus field will be denoted by three collections of quantum numbers:

\[ |\nu, n, \alpha\rangle \] (6)
\( \nu \) comes for the internal state of the absorber, \(|n\rangle = |n_1, n_2, \ldots\rangle\) denotes the occupation numbers of all
the radiation modes and $\alpha$ is the collection of bath quantum numbers. Out of the infinite number of the radiation field modes we shall normally focus on one or two and the rest may be assumed to be in the vacuum state. $n$ will therefore be allowed to assume only a few values. It is convenient to define a combined state of the absorber plus the field [16–18]:

$$|\nu\rangle = |\tilde{\nu}, n\rangle.$$  \hspace{1cm} (7)

In each application we shall first of all have to identify the relevant values of $n$ (and $|\nu\rangle$). This will be made clear throughout the present work. We should reiterate that $|\tilde{\nu}\rangle$ are eigenstates of $\tilde{H}_0$, $|n\rangle$ are the eigenstates of $H_R$ and $|\nu\rangle$ are therefore eigenstates of $\tilde{H}_0 + H_R$.

3. The description of multiphoton processes using the tetradic $\mathcal{T}$ matrix

In this section we shall introduce the basic theoretical tool which allows us to describe all radiative stationary processes in a unified and systematic way, namely the tetradic (Liouville space) $\mathcal{T}$ matrix. Let us first define the Liouville space. In this space we define a ket vector $|A\rangle$ corresponding to an ordinary operator $A$ and a bra $\langle A|$ corresponding to its hermitian conjugate $A^\dagger$. The Liouville equation,

$$\frac{dA}{dt} = i[H, A]$$ \hspace{1cm} (8)

can be written in a tetradic matrix form [57]:

$$\frac{dA_{nm}}{dt} = i \sum_{k,l} L_{nm,kl} A_{kl}$$ \hspace{1cm} (9)

where

$$L = [H, ].$$ \hspace{1cm} (10)

Upon comparing equations (8) and (9) we have:

$$L_{nm,kl} = H_{nk}\delta_{ml} - H_{ml}^*\delta_{nk}.$$ \hspace{1cm} (11)

We further define a scalar product in Liouville space

$$\langle\langle A|B\rangle\rangle = \text{Tr}(A^\dagger B)$$ \hspace{1cm} (12)

and a tetradic “matrix element”

$$\langle\langle A|L|B\rangle\rangle = \text{Tr}(A^\dagger LB).$$ \hspace{1cm} (13)

For each part of the Hamiltonian $H_1$, $H_0$, $H_M$, $V$ etc. we define a corresponding Liouvillian $L_1$, $L_0$, $L_M$, $V$ etc. defined in an analogous form to equation (10), e.g. $L_0 = [H_0, ]$, $V = [V, ]$ etc. Suppose we start at time ($t \rightarrow -\infty$) with matter plus the radiation field which are non interacting ($V = 0$). The total density
matrix will be
\[ \rho(-\infty) = \rho_M(-\infty) \rho_R(-\infty). \] (14)

If \( V \) is adiabatically switched on, we have at steady state:
\[ \rho(t = 0) = [1 + G(\omega = 0) V] \rho(-\infty) \] (15)
where
\[ G(\omega) = \frac{1}{\omega - L + i\epsilon} \] (16)
is the tetradic Green’s function. Equation (15) is the analogue of the Lippman–Schwinger equation of scattering theory [58]. We shall be interested in detecting the rate of radiative change of an operator \( A \)
\[ \langle \dot{A}\rangle = \frac{d\langle A\rangle}{dt} = i\mathcal{T}(\omega = 0) \rho(-\infty) \] (17)
Using equations (14)–(17) we get at steady state:
\[ \langle \dot{\rho}(0) \rangle = -i\langle [A, \mathcal{T}(\omega = 0) \rho(-\infty)] \rangle \] (18)
where
\[ \mathcal{T}(\omega) = V + \mathcal{V} - \frac{1}{\omega - L + i\epsilon} \mathcal{V} = V + \mathcal{V} G(\omega) \mathcal{V}. \] (19)

Equation (18) together with (19) is the basic equation to be used throughout the present work. It allows us to describe the cross section for any multiphoton process associated with the Hamiltonian (1) as an appropriate matrix element of the tetradic \( T \) matrix \( \mathcal{T} \). \( \mathcal{T} \) is the tetradic analogue of the ordinary \( T \) matrix commonly used in scattering theory [58],
\[ T(E) = V + V \frac{1}{E + H + i\epsilon} V. \] (20)

We shall now consider several formal properties of \( \mathcal{T} \). Let us first of all take \( A \) to be the unit operator
\[ A = 1 = \sum_{\nu} |\nu\rangle \langle \nu| \] (21)
and
\[ \rho(-\infty) = |a\rangle \langle a| \rho_a(Q). \] (22)
Here
\[ \rho_a(Q) = \exp(-H_a/k\tilde{T})/\text{Tr} \exp(-H_a/k\tilde{T}), \] (23)
$\bar{T}$ is the temperature, and $\rho_a$ is the density matrix of the perturbers. In Liouville (tetradic) notation one may rewrite eqs. (21) and (22) in the form:

\begin{equation}
|1\rangle = \sum_\nu |\nu\rangle
\end{equation}

\begin{equation}
|\rho(-\infty)\rangle = \rho_a|aa\rangle.
\end{equation}

Upon substitution of eqs. (23) and (24) in eq. (18) and since the unit operator commutes with any other operator, i.e.

\begin{equation}
\langle 1|V = 0,
\end{equation}

we get

\begin{equation}
\langle 1|\mathcal{T}(\omega) \rho_a|aa\rangle = 0.
\end{equation}

Using eqs. (26) and (24), we finally have

\begin{equation}
\sum_\nu \langle \nu\nu|\mathcal{T}(\omega) \rho_a|aa\rangle = 0
\end{equation}

i.e.

\begin{equation}
\langle aa|\mathcal{T}(\omega) \rho_a|aa\rangle = -\sum_\nu \langle \nu\nu|\mathcal{T}(\omega) \rho_a|aa\rangle.
\end{equation}

The relation between the matrix elements of the tetradic and ordinary (dyadic) $T$ matrix is [38, 39]:

\begin{equation}
\langle \nu'\nu'|\mathcal{T}(0)|\nu\nu\rangle = [T_{\nu\nu}(E_\nu) - T_{\nu'\nu}(E_\nu)] \delta_{\nu\nu'} + 2\pi i |T_{\nu'\nu}(E_\nu)|^2 \delta(E_\nu - E_{\nu'}).\n\end{equation}

Upon substitution of eq. (28) in eq. (27b) we get

\begin{equation}
-\text{Im}(T_{aa}(E_a)) = \pi \sum_{\nu \neq a} |T_{\nu a}(E_a)|^2 \delta(E_\nu - E_a)
\end{equation}

where $\langle \ldots \rangle$ comes for the averaging over the bath degrees of freedom.

We have thus shown that eq. (27) is nothing but the optical theorem of scattering theory [58] rewritten in tetradic notation.

We are now in a position to develop the perturbative series for $\mathcal{T}$. To that end we introduce the following Green's functions:

\begin{equation}
G_s(\omega) = \frac{1}{\omega - L_{\nu a} + i\epsilon} = -i \int_0^\infty d\tau \exp(i\omega \tau) G_s(\tau)
\end{equation}
where
\[ G_s(\tau) = \exp(-iL_s\tau). \] (31)

Similarly we have:
\[ \bar{G}_s(\omega) = \frac{1}{\omega - \bar{L}_s + i\epsilon}. \] (32)
\[ G_1(\omega) = \frac{1}{\omega - \bar{L}_1 + i\epsilon}. \] (33)

Making use of the Dyson equation [56] we immediately have from eqs. (19) and (30)
\[ \mathcal{F}(\omega) = \mathcal{V} + \sum_{n=2}^{\infty} \mathcal{F}^{(n)}(\omega) \] (34)
\[ \mathcal{F}^{(n)}(\omega) = [\mathcal{V} G_s(\omega)]^{n-1} \mathcal{V}. \] (35)

\( \mathcal{F}^{(n)}(\omega) \) is to n-th order in \( \mathcal{V} \). Since in all our applications the physical observables are obtained using even orders of \( \mathcal{V} \), we shall hereafter consider \( \mathcal{F}^{(2n)} \). In the time domain we may rewrite eq. (35) in the form:
\[
\mathcal{F}^{(2n)}(\omega) = -i \int_0^\infty dt_1 \int_0^\infty dt_2 \cdots \int_0^\infty dt_{2n-1} \exp(i\omega t_1)
\times \mathcal{V} G_s(t_1-t_2) \mathcal{V} G_s(t_2-t_3) \cdots G_s(t_{2n-2}-t_{2n-1}) \mathcal{V} G_s(t_{2n-1}) \mathcal{V}.
\] (36b)

Since \( L_1 \) and \( \bar{L}_s \) commute and since \( L_1\rho(-\infty) = L_1|\nu\nu\rangle = 0 \), we may write the matrix elements of \( \mathcal{F} \) in the form:
\[
\sigma_{av} = -i \langle \nu\nu| \mathcal{F}^{(2n)}(0) \rho_a|\nu\nu\rangle
= (-i)^n \int_0^\infty dt_1 \int_0^\infty dt_2 \cdots \int_0^\infty dt_{2n-1} \langle \nu\nu| \mathcal{V}(t_1) \bar{G}_s(t_1-t_2) \mathcal{V}(t_2)
\times \bar{G}_s(t_2-t_3) \cdots \bar{G}_s(t_{2n-2}-t_{2n-1}) \mathcal{V}(t_{2n-1}) \bar{G}_s(t_{2n-1}) \mathcal{V}(0) \rho_a|\nu\nu\rangle.
\] (37)
where

\[ V(t) = \exp(iL_1 t) \exp(-iL_1 t). \]  

(38)

Alternatively we may use the ordinary \( T \) matrix (eq. (20)) together with eq. (22) and get

\[ \langle \nu \nu | \mathcal{F}(0) \rho_{aa} | \nu \nu \rangle = 2\pi i \text{Tr}_B \{ T_{aa}(E_a) \rho_a T_{aa}^+(E_a) \delta(E_a - H) \} \]  

(39)

i.e.

\[ \langle \nu \nu | \mathcal{F}^{(2n)}(0) \rho_{aa} | \nu \nu \rangle = 2\pi i \text{Tr}_B \sum_{p=0}^{2n} \langle \nu | T^{(p)}(E_a) | a \rangle \rho_a \langle a | T^{+(2n-p)}(E_a) \delta(E_a - H) | \nu \rangle. \]  

(40)

Here \( T^{(p)} \) is analogous to \( \mathcal{F}^{(p)} \) and may be evaluated using eqs. (34)–(36) via the substitution \( \mathcal{V} \to V \) and \( G_a(\tau) \to \exp(-iH_a \tau) \). The sum in eq. (40) is over all the possibilities of applying \( p \) perturbations from the left and \( 2n - p \) perturbations from the right to get an overall expression to order \( 2n \). Eq. (40) is a rearrangement of eq. (37) and provides an alternative bookkeeping device. Eq. (37) is fully time ordered \( (t_1 > t_2 \cdots > t_{2n-1}) \) and keeps track of the order in time in which the various perturbations are applied. Using the relation \( \mathcal{V} = [V \cdots] \), eq. (37) results in a sum of all sequences in time in which we can apply \( 2n \) perturbations. In eq. (40), on the other hand, we keep track of the total number of left \( (p) \) and right \( (2n-p) \) perturbations and we disregard the relative order in time of the left and right perturbations. Of course, the final result is the same whether we use eq. (37) or (40).

Eq. (37) is our fundamental equation and this entire article is devoted to its evaluation under different conditions. The details will be presented in the coming sections. We shall however sketch the essential steps inherent in that evaluation here. Let us consider a common situation in multiphoton experiments in which a strong, single mode, laser field is interacting with a multilevel system and couples successive states, i.e.

\[ |a\rangle = |\tilde{a}, \tilde{n}\rangle \]  

(41a)

\[ |b\rangle = |\tilde{b}, \tilde{n} - 1\rangle \]  

(41b)

\[ |c\rangle = |\tilde{c}, \tilde{n} - 2\rangle \]  

(41c)

\[ \vdots \]

Here \( |a\rangle \) is coupled by \( \mu \) to \( |b\rangle \), \( |b\rangle \) to \( |a\rangle \) and \( |c\rangle \) etc. The states \( |a\rangle, |b\rangle, |c\rangle \ldots \) thus form a “linear chain” of coupled states. The coupling scheme is shown in fig. 1. In an \( n \) photon process, we go from \( |aa\rangle \) to \( |\nu \nu\rangle \) by absorbing \( n \) photons \( (\nu = b, c, \ldots \) for \( n = 1, 2, \ldots \) respectively). The appropriate operator which should be considered is \( \mathcal{F}^{(2n)} \) since it is the lowest order in which we can go from \( |aa\rangle \) to \( |\nu \nu\rangle \). (We need \( \mathcal{F}^{(2)} \) for a single photon process, \( \mathcal{F}^{(4)} \) for a two photon process, etc.) We next ask how many pathways with \( 2n \) lines do exist which lead from \( |aa\rangle \) to \( |\nu \nu\rangle \). A simple inspection of fig. 1 shows that for \( \nu = b, c \) and \( d \) \( (n = 1, 2, 3) \) there are 2, 6 and 20 pathways respectively. It may easily be verified that for an \( n \) photon process we have \( (2n)!/(n!)^2 \) pathways. (We have to operate with \( \mathcal{V} \) \( n \) times from the left and \( n \) times from the right in all possible sequences and this results in the above combinatorial factor.)
Fig. 1. The pathways in Liouville space which contribute to the multiphoton cross section (eq. (37)). Each bond denotes a radiative coupling $\lambda$. For an $n$ photon process we need consider the $(2n)!/(n!)^2$ pathways which start from $\alpha\beta\cdots\gamma$ and end at $\nu\mu\cdots\eta$. The pathways always come in complex conjugate pairs obtained by the transformation $\alpha\beta\cdots\gamma \rightarrow \tilde{\alpha}\tilde{\beta}\cdots\tilde{\gamma}$ for all the points in the pathway. The states lying along the broken lines are “even” and appear in the projection operator $\hat{P}$ (eq. (43a)) which is used to construct the factorization approximation.

Using the Liouville conjugation symmetry [38, 39]

$$G_{k,l,m,n}(0) = -G^*_{l,k,m,n}(0)$$

we see that for each pathway there is a complex conjugate pathway obtained by using the transformation $kl \leftrightarrow lk$ for all points along the path. Therefore we need actually calculate only $(2n)!/(2(n!)^2)$ pathways (and take the imaginary part). The basic procedure for the calculation of an $n$ photon process involves therefore the following steps:

(i) Identify the $n + 1$ relevant matter plus radiation states $|a\rangle$, $|b\rangle$, $|c\rangle$, $\ldots$, $|\nu\rangle$.

(ii) Using fig. 1 identify the $(2n)!/(2(n!)^2)$ independent pathways which lead from $|\alpha\alpha\rangle$ to $|\nu\nu\rangle$.

(iii) For each pathway identify the phase factors $\tilde{G}_\nu$ and write the appropriate correlation function (eq. (37)).

(iv) Evaluate the correlation function by one of the available methods (cluster, perturbative, stochastic, semiclassical, etc.).

In concluding this section we shall introduce the factorization approximation which is very useful in many cases. As we see from eq. (37), the honest evaluation of the cross section for an $n$ photon process involves the calculation of a $2n$-time correlation function, followed by $2n - 1$ time integrations. Both of these steps are very complicated. In many cases the information content of the experiment is much less detailed than the complete information contained in the $2n$ time correlation function. A useful simple approximation may be obtained as follows: We define the tetradic Mori projection operators [57, 59]:

$$\hat{P} = \sum_{\nu,\mu} |A_{\nu}\rho_{\nu}\rangle S_{\nu,\mu}^{-1}\langle A_{\mu}|$$

$$\hat{Q} = 1 - \hat{P}.$$
The set $|A_\nu\rangle$ is a partial set of system operators which should be sufficient to represent $\rho(-\infty)$ as well as our final observable $|\nu\rangle\rangle$, i.e. $\hat{P}\rho(-\infty)\rangle\rangle = |\rho(-\infty)\rangle\rangle$, $\hat{P}|\nu\rangle\rangle = \rho_\nu|\nu\rangle\rangle$.

$S_{\rho_\nu}$ is the “overlap” of $A_\nu$ and $A_{\nu}\rho_\nu$ in Liouville space, i.e.

$$S_{\rho_\nu} = \text{Tr}(A_\nu^\dagger A_{\nu}\rho_\nu) ;$$  \hspace{1cm} (43c)

$\rho_\nu$ is the bath density operator. The simplest choice is $\rho_\nu = \rho_\nu$ (eq. (23)) although more elaborate choices will be made later (see eqs. (194), (213) and (236)). A convenient choice for $A_\nu$ is to take all “even” operators (those lying along the broken lines in fig. 1, which may be reached via the application of even powers of $V$ to $|aa\rangle\rangle$). We then make use of the following formally exact expression [58]:

$$\hat{P}\mathcal{I}(\omega)\hat{P} = \hat{P} R(\omega) \hat{P} (1 - \hat{P} G_\nu(\omega) \hat{P} R(\omega) \hat{P})^{-1}$$  \hspace{1cm} (44a)

where

$$R(\omega) = V + VQ \frac{1}{\omega - QLQ} \hat{Q}V.$$  \hspace{1cm} (44b)

The significance of eqs. (44) is as follows: Instead of evaluating $\mathcal{I}(\omega)$, we evaluate $R(\omega)$ approximately. Upon substitution of $R(\omega)$ in (44a) we get an approximation for $\mathcal{I}(\omega)$. A low order approximation for $R(\omega)$ results in an infinite order approximation for $\mathcal{I}(\omega)$. Eqs. (44), therefore, correspond to a partial resummation of the perturbative series (34) for $\mathcal{I}$. Upon expanding $R$ to second order we have:

$$\hat{P} R^{(2)}(\omega) \hat{P} = \hat{P} V \hat{P} + \hat{P} VQ G_\nu(\omega) \hat{Q} V \hat{P}.$$  \hspace{1cm} (45)

For the choice of $\hat{P}$ discussed previously (see fig. 1), we have $\hat{Q} V \hat{P} = V \hat{P}$ so that

$$\hat{P} R^{(2)}(\omega) \hat{P} = \hat{P} \mathcal{I}^{(2)}(\omega) \hat{P} = \hat{P} V G_\nu(\omega) V \hat{P}.$$  \hspace{1cm} (46)

We thus have:

$$\hat{P} \mathcal{I} \hat{P} = \hat{P} \mathcal{I}^{(2)} \hat{P} (1 - \hat{P} G_\nu \hat{P} \mathcal{I}^{(2)} \hat{P})^{-1}.$$  \hspace{1cm} (47)

If we now expand this to 2nth order we get

$$\hat{P} \mathcal{I}^{(2n)} \hat{P} = \hat{P} \mathcal{I}^{(2)} \hat{P} (\hat{P} G_\nu \hat{P} \mathcal{I}^{(2)} \hat{P})^{n-1}$$  \hspace{1cm} (48)

or alternatively

$$\hat{P} \mathcal{I}^{(2n)} \hat{P} = (\hat{P} V G_\nu V \hat{P} G_\nu \hat{P})^{n-1} \hat{P} V G_\nu V \hat{P}.$$  \hspace{1cm} (49)

The lowest order approximation thus gives us an expression for multiphoton processes in terms of products of single photon line shapes $\hat{P} \mathcal{I}^{(2)} \hat{P}$ and $PG_\nu \hat{P}$ (eq. (48) or (49)).

If we further invoke the Markov (impact) approximation, we replace the $PG_\nu \hat{P}$ matrix by
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\[ \hat{P} G_s(\omega) \hat{P} = (\omega - \tilde{L}_e - L_R + i\Gamma)^{-1} \]  

where \( \Gamma \) is a relaxation matrix which contains \( T_1 \) and \( T_2 \) contributions (see eq. (130)). Eq. (49) together with (49a) is the result obtained using the Bloch equations. This limit will be discussed in detail later. At this stage we just wish to emphasize that the Bloch equations are equivalent to applying the factorization (49) plus impact (49a) approximations to the exact expression (eq. (37)).

4. Single photon processes – Absorption line shapes

In this section we shall consider the simplest radiative process, i.e. a two level system \( \vec{\nu} = \vec{\alpha}, \vec{\beta} \) interacting with a single mode of the radiation field occupied with \( n_L \) photons with frequency \( \omega_L \). We assume that \( \omega_{ba} = \varepsilon_b - \varepsilon_a \gg kT \) so that

\[ \rho_m(-\infty) = |\vec{\alpha}\rangle\langle\vec{\alpha}| \cdot \rho_a(Q) \]  

where \( \rho_a(Q) \) was defined in eq. (23). The relevant system (matter plus radiation) states will be

\[ |a\rangle = |\vec{\alpha}, n_L\rangle , \]  

\[ |b\rangle = |\vec{\beta}, n_L - 1\rangle , \]  

so that

\[ \rho(-\infty) = \rho_m(-\infty) \rho_r(-\infty) = |a\rangle \langle a| \rho_a(Q) . \]  

We further introduce the definitions

\[ \Delta = \omega_L - \omega_{ba} \]  

\[ \mu_L \equiv |\mu_{ba}| . \]  

The absorption line shape from \( |a\rangle \) to \( |b\rangle \) is given by (see eq. (37)):

\[ \sigma_{ab}(\Delta) = \frac{i}{2\pi\mu_L^2} \langle \langle bb \rangle \mathcal{F}^{(2)}(0) \rho_a | aa \rangle \rangle = \frac{i}{2\pi\mu_L} \langle \langle aa \rangle \mathcal{F}^{(2)}(0) \rho_a | aa \rangle \rangle = \frac{i}{2\pi} \left[ \langle \langle ab \rangle \mathcal{G}_s(0) \rho_a | ab \rangle \rangle + \langle \langle ba \rangle \mathcal{G}_s(0) \rho_a | ba \rangle \rangle \right] \]

where the \( 2\pi\mu_L^2 \) factor was introduced for the sake of normalization, i.e.

\[ \int \sigma_{ab}(\Delta) \, d\Delta = 1 . \]
As is clearly seen from fig. 2 we need evaluate only one pathway (plus its complex conjugate path) in this case. We therefore define the contribution of the pathway that passes via $|ab\rangle$ (the first term in the brackets of eq. (55)) as:

$$I_{ab}(\Delta) = \langle \langle ab|G_x(0)\rho_a|ab\rangle \rangle = -i \int_0^\infty d\tau \exp(-i\Delta \tau - \frac{1}{2}\gamma \tau) I_{ab}(\tau) = I_{ab}(\Delta) - i I_{ab}'(\Delta)$$

where

$$\mu_L^2 I_{ab}(\tau) = \text{Tr}(V_{ab}(\tau) V_{ba}(0)\rho_a) \equiv \langle V_{ab}(\tau) V_{ba}(0) \rangle.$$  

Using eqs. (1c) and (58) we get

$$I_{ab}(\tau) = \text{Tr}[\exp(iH_a\tau) \exp(-iH_b\tau) \rho_a]$$

so that

$$\sigma_{ab}(\Delta) = \frac{1}{\pi} I_{ab}'(\Delta).$$

The function $I_{ab}(\Delta)$ is the single photon line shape function. Its real and imaginary parts are related by the Kramers–Kronig relation [58]

$$I_{ab}'(\Delta) = -\frac{1}{\pi} \text{PP} \int d\Delta' \frac{I_{ab}(\Delta')}{\Delta - \Delta'}.$$

Therefore the absorption line shape $I_{ab}'$ is sufficient to determine $I_{ab}(\Delta)$. Note also that $I_{ab}(\Delta) = -I_{ba}'(-\Delta)$. We shall now consider various methods for the evaluation of $I_{ab}(\Delta)$.

4.1. The dressed cluster expansion

The purpose of the cluster expansion is to express the line shape in terms of the dynamics of small clusters of atoms (one perturber, two perturbers, etc.). We shall develop here a “dressed cluster
expansion" DCE which retains the exact static information (i.e., \( n \)-particle static correlation functions) of the material system [42, 43]. The usefulness of the DCE arises since the line shape is easily calculable in terms of well known quantities (static correlations plus few body dynamics).

We start by rearranging \( I_{ab}(\tau) \) eq. (59)) in the form:

\[
I_{ab}(\tau) = \langle 1 + f_{ab}(\tau) \rangle ,
\]

where

\[
f_{ab}(\tau) \equiv \exp(iH_a\tau) \exp(-iH_b\tau) - 1 .
\]

The \( \langle \cdots \rangle \) operation was defined in eq. (58). \( f_{ab}(\tau) \) has the desirable property that it vanishes when all particles are far apart. We next partition the Hamiltonian eq. (3) as follows:

\[
H_a \equiv H_0 + U_a ,
\]

\[
H_b \equiv H_0 + U_b ,
\]

where

\[
H_0 \equiv T_0 + \sum_p T_p ,
\]

\[
U_a \equiv \sum_p U_a^{sp} + \sum_{p>p'} U_{pp'} ,
\]

and

\[
U_b \equiv \sum_p U_b^{sp} + \sum_{p>p'} U_{pp'} .
\]

Let us introduce the positive and negative time ordered exponentials, as follows:

\[
\exp(-iH_0\tau) = \exp(-iH_0\tau) \exp \left[ -i \int_0^\tau d\tau_1 U_b(\tau_1) \right] \]

\[
\exp(iH_a\tau) = \exp \left[ i \int_0^\tau d\tau_1 U_a(\tau_1) \right] \exp(iH_0\tau)
\]

where

\[
A(\tau) \equiv \exp(iH_0\tau) A \exp(-iH_0\tau) , \quad A = U_a, U_b
\]

\[
\exp \left[ -i \int_0^\tau d\tau_1 A(\tau_1) \right] = 1 - i \int_0^\tau d\tau_1 A(\tau_1) + (-i)^2 \int_0^\tau d\tau_1 \int_0^\tau d\tau_2 A(\tau_1) A(\tau_2) + \cdots
\]
To simplify our subsequent manipulations we shall define the time ordering operators $T_b^+$ and $T_a^-$ as follows: $T_b^+(T_a^-)$ which operates on a product of $U_b(U_a)$ at different times, rearranges them in order of decreasing (increasing) times from left to right, i.e.

\[
T_b^+ U_b(\tau_1) U_b(\tau_2) \cdots U_b(\tau_k) = U_b(\tau_1) U_b(\tau_2) \cdots U_b(\tau_k) \\
T_a^- U_a(\tau_1) U_a(\tau_2) \cdots U_a(\tau_k) = U_a(\tau_k) U_a(\tau_{k-1}) \cdots U_a(\tau_1)
\]

$\tau_1 > \tau_2 \cdots > \tau_k$

$\tau_1 \cdots \tau_k$ is a permutation of $\tau'_1 \cdots \tau'_k$. We thus have:

\[
1 + f_{ab}(\tau) = 1 + T_b^+ T_a^- \exp\left[ \int_0^\tau d\tau_1 U_a(\tau_1) \right] \exp\left[ -i \int_0^\tau d\tau_1 U_b(\tau_1) \right].
\]

To proceed further we shall now introduce the functions:

\[
f_{jk}^{ab}(\tau) = \exp\left[ \int_0^\tau d\tau_1 U_a^{jk}(\tau_1) \right] \exp\left[ -i \int_0^\tau d\tau_1 U_b^{jk}(\tau_1) \right] - 1
\]

where $j$ and $k$ run over the absorber as well as the perturbers $j, k = s, 1, \ldots N$. In addition let us introduce a third ordering operator $T^*$. When $T^*$ operates on a product of $U_a$ and $U_b$ terms it rearranges them such that all $U_a$ are to the left and all $U_b$ are to the right. We can now define:

\[
\hat{T}_{ab} = T_a^- T_b^+ T^*
\]

so that

\[
1 + f_{ab}(\tau) = \hat{T}_{ab} \prod_{j,k = 1}^{N+1} [1 + f_{jk}^{ab}(\tau)].
\]

Eq. (73) is an important starting point for the cluster expansion.

We now define $I_p(\tau)$ as the dressed $p$ perturber spectrum. It is calculated for a system consisting of the absorber atom $+ p$ perturbers in a volume $\Omega$. The "dressing" is reflected in the fact that for the distribution function we use the reduced $p + 1$ particle distribution function of the system [60]

\[
\phi_{p+1}(X_s, X_1, X_2, \ldots X_p) \equiv \frac{\text{Tr}}{p+1, \ldots N} \rho_s(X_s, X_1, \ldots X_N)
\]

where

\[
X_\alpha \equiv (Q_\alpha, P_\alpha).
\]
Eq. (74) is valid both classically where $Q_\alpha$, $P_\alpha$ are classical coordinates, and quantum mechanically where $Q_\alpha$, $P_\alpha$ are operators. $\phi_{p+1}$ should be distinguished from the bare cluster distribution function $\phi_{p+1}^0$ defined for a system with one absorber and $p$ perturbers which is commonly used in the ordinary cluster expansions (OCE) of line broadening [41]:

$$\phi_{p+1}^0(X_s, X_1, \ldots X_p) = \exp[-\beta H_a^{(p+1)}(X_s, X_1, \ldots X_p)]/Z^{(p+1)}$$

(76a)

where

$$Z^{(p+1)} = \text{Tr} \exp[-\beta H_a^{(p+1)}(X_s, X_1, \ldots X_p)].$$

(76b)

Here the superscript $(p+1)$ denotes that the system contains only $p+1$ particles. We thus define:

$$I_p(\tau) \equiv \text{Tr}\{\exp(iH_a^{(p+1)}\tau)\exp(-iH_b^{(p+1)}\tau) \phi_{p+1}\}. \quad (77)$$

Using these definitions we may rewrite eq. (77) in the form:

$$I_p(\tau) = \text{Tr}\left\{ \hat{T}_{ab} \prod_{j,k=1}^{p+1} [1 + f_{ab}^{jk}(\tau)] \rho_a \right\}. \quad (78)$$

Eq. (78) is our starting point for the cluster expansion. To proceed further we shall consider the series of $p$ perturber spectra $I_p$:

$$I_0 = 1$$

(79a)

$$I_1 = 1 + \langle f_{ab}^1 \phi_2(X_s, X_1) \rangle \equiv 1 + \frac{1}{\Omega} \chi_1$$

(79b)

$$I_2 = 1 + \left[ \langle f_{ab}^1 \phi_2(X_s, X_1) \rangle + \langle f_{ab}^2 \phi_2(X_s, X_2) \rangle \right] + \left[ \langle f_{ab}^1 f_{ab}^2 \phi_3(X_s, X_1, X_2) \rangle \right]$$

$$+ \langle f_{ab}^1 f_{ab}^2 f_{ab}^1 \phi_3(X_s, X_1, X_2) \rangle + \langle f_{ab}^2 f_{ab}^2 \phi_3(X_s, X_1, X_2) \rangle

+ \langle f_{ab}^1 f_{ab}^2 f_{ab}^1 \phi_3(X_s, X_1, X_2) \rangle \equiv 1 + \frac{2}{\Omega} \chi_1 + \frac{1}{\Omega^2} \chi_2.$$  

(79c)

Here $\Omega$ is the volume, $\phi_{p+1}(X_s, X_1, \ldots X_p)$ is the reduced $p+1$ particle distribution function (eq. (74)) and

$$\langle f_{ab}^{u_l} f_{ab}^{v_l} \ldots \phi_{p+1} \rangle \equiv \hat{T}_{ab} \prod_{s,1 \ldots p} \langle f_{ab}^{u_l} f_{ab}^{v_l} \ldots \phi_{p+1} \rangle. \quad (80)$$

A pictorial representation of the two perturber spectrum $I_2$ (eq. (79c)) is displayed in fig. 3. The six terms in (79c) are represented by diagrams showing which atoms are interacting. In eq. (79) each term containing $k$ different atoms requires them to be microscopically close and is thus $O(1/\Omega^k).$ It is easy to see
that the general term $I_p$ will be given by:

$$I_p = 1 + \sum_{k=1}^{p} \frac{1}{\Omega^k} \binom{p}{k} \chi_k$$

(81)

the $k$th contribution is of the \(\binom{p}{k}\) clusters of $k$ perturbers. Eqs. (81) may be inverted to yield:

$$\chi_1 = \Omega(I_1 - 1),$$

$$\chi_2 = \Omega^2(I_2 - 2I_1 + 1),$$

$$\chi_p = \Omega^p[I_p - \binom{p}{1} I_{p-1} + \binom{p}{2} I_{p-2} - \cdots] .$$

(82)

In the thermodynamic limit we consider $N$ perturbers where \(N \to \infty\), \(\Omega \to \infty\) and \(N/\Omega\) is finite. We then have:

$$\binom{N}{q} \frac{1}{\Omega^q} \to \frac{n^q}{q!} ,$$

(83)

where

$$n = N/\Omega .$$

(84)

Upon substitution of eq. (83) in eq. (81) we get in the thermodynamic limit:

$$I_{ab}(\tau) = 1 + \sum_{q=1}^{\infty} \frac{n^q}{q!} \chi_q(\tau) .$$

(85)

The final step in the DCE is made by introducing the ansatz
\[ I_{ab}(\tau) = \exp\left[ \sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(\tau) \right]. \]  

(86)

\( J_q \) may be obtained by equating the expansions (85) and (86) term by term, i.e.

\[ \sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(\tau) = \log \left[ 1 + \sum_{q=1}^{\infty} \frac{n^q}{q!} \chi_q(\tau) \right]. \]  

(87)

Using eq. (87), \( J_q(\tau) \) will be expressed in terms of \( \chi_q(\tau) \) where \( q' \leq q \), i.e.

\[
\begin{align*}
J_1(\tau) & = \chi_1, \\
J_2(\tau) & = \chi_2 - \chi_1^2, \\
J_3(\tau) & = \chi_3 - 3\chi_2\chi_1 + 2\chi_1^3, \text{ etc.}
\end{align*}
\]

(88a) (88b) (88c)

In concluding this section we note the following:

1. Eq. (86) with (88) is our final result for the DCE expansion. \( J_p \) are given in terms of the \( p \)-perturbers spectrum \( I_p \). The \( p \)th order DCE is obtained by calculating the spectrum of our absorber plus \( p \)-perturbers eq. (77) using the static distribution functions (74). We then get \( \chi_1, \ldots, \chi_p, J_1, \ldots, J_p \) are obtained from \( \chi_1, \ldots, \chi_p \) using eqs. (88).

2. An alternative cluster expansion is the ordinary cluster expansion (OCE). The OCE is obtained by simply replacing each \( \phi_p \) in eq. (79) by \( \phi^0_p \), the “bare” \( p \)-particle static distribution function. Both the DCE and the OCE are formally exact, however the DCE is a resummed version of the OCE and a low-order DCE contains many terms (i.e. static contributions often called “initial correlations”) \[55\] which appear in the OCE in higher orders.

3. The exactly solvable Anderson–Talman \[31\] model is defined by taking \( U^{pp'} = 0 \) in eq. (3), i.e. the bath atoms do not interact with each other but only interact with the absorber. For this model it is easy to show that \( J_q(\tau) \) with \( q \geq 2 \) vanish identically and we have the exact result:

\[ I_{ab}(\tau)^{\text{(AT)}} = \exp[nJ_1(\tau)]. \]  

(89)

4.2. The perturbative expansion

We shall now develop an alternative expansion for \( I_{ab}(\tau) \) this time in terms of dynamic correlation functions of the fluid \[42\]. The latter may then be evaluated using kinetic or hydrodynamic techniques \[60, 61\]. Let us define the perturbation responsible for the line broadening:

\[ \lambda U = H_b - H_a = \sum_p U^{sp}, \]  

(90)

where

\[ U^{sp} = U_b^{sp} - U_a^{sp}. \]  

(91)
We may then write:

\[
\exp(-iH_0 \tau) = \exp(-iH_a \tau) \exp\left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1)\right],
\]

(92)

where

\[
U(\tau) = \exp(iH_a \tau) U \exp(-iH_a \tau),
\]

(93)

and where \(\exp_+\) was defined in eq. (68).

Upon substituting eq. (92) in eq. (59) we get:

\[
I_{ab}(\tau) = \left\langle \exp\left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1)\right] \rho_a \right\rangle.
\]

(94)

For the subsequent manipulations let us introduce the following moments:

\[
m_p(\tau_1, \ldots, \tau_p) = \left\langle U(\tau_1) \cdot U(\tau_2) \cdots U(\tau_p) \right\rangle \\
= \text{Tr}\{U(\tau_1) U(\tau_2) \cdots U(\tau_p) \rho_a\}.
\]

(95)

Alternatively if we introduce the Fourier representation:

\[
U(Q) = \sum_k \exp(ikQ) U_k
\]

(96)

and

\[
N_k = \sum_p \exp(ik \cdot Q_p),
\]

\[
\hat{N}_k = \exp(ik \cdot Q_a),
\]

(97a)

(97b)

we have

\[
m_p(\tau_1, \tau_2, \ldots, \tau_p) \sum_{k_1 k_2 \ldots k_p} U_{k_1} U_{k_2} \cdots U_{k_p} \left\langle \hat{N}_{k_1}(\tau_1) N_{-k_1}(\tau_1) \hat{N}_{k_2}(\tau_2) N_{-k_2}(\tau_2) \cdots \hat{N}_{k_p}(\tau_p) N_{-k_p}(\tau_p) \right\rangle.
\]

(98)

Here \(N_k\) is the particle number density and \(\hat{N}_k\) is the density of a tagged particle.

We note that \(m_1 = \left\langle U \right\rangle\) is time independent. Without loss of generality, we may include \(\left\langle U \right\rangle\) in \(\omega_{ba}\) i.e. use the transformation:

\[
\omega_{ba} \rightarrow \omega_{ba} + \left\langle U \right\rangle
\]

(99a)
so that:

\[ m_1 = 0 . \]  

Using eqs. (94), (95) and (99) we get:

\[
I_{ab}(\tau) = 1 + (-i\lambda)^2 \int_0^\tau d\tau_2 \int_0^{\tau_1} d\tau_1 m_2(\tau_1, \tau_2) + (-i\lambda)^3 \int_0^\tau d\tau_2 \int_0^{\tau_1} d\tau_1 \int_0^{\tau_2} d\tau_3 m_3(\tau_1, \tau_2, \tau_3) + \cdots
\]

The final step in the perturbative expansion is to introduce the ansatz:

\[
I_{ab}(\tau) = \exp\left[ \sum_{q=1}^\infty (-i\lambda)^q K_q(\tau) \right],
\]

\[ K_q(\tau) \] are obtained by expanding eq. (101) in \( \lambda \) and comparing term by term with eq. (100) resulting in:

\[
\sum_{q=1}^\infty (-i\lambda)^q K_q(\tau) \equiv \log\left\{ 1 + \left[ \exp\left\{ -i\lambda \int_0^\tau d\tau_1 U(\tau_1) \right\} - 1 \right] \right\}
\]

i.e.

\[
K_1 = 0 ,
\]

\[
K_2 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 m_2(\tau_1, \tau_2),
\]

\[
K_3 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 m_3(\tau_1, \tau_2, \tau_3),
\]

\[
K_4 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \left[ m_4(\tau_1, \tau_2, \tau_3, \tau_4) - m_2(\tau_1, \tau_2) m_2(\tau_3, \tau_4) - m_2(\tau_1, \tau_3) m_2(\tau_2, \tau_4) - m_2(\tau_1, \tau_4) m_2(\tau_2, \tau_3) \right].
\]

Eq. (101) together with (103) is our final result for the perturbative expansion [42].

4.3. Practical methods for the calculation of single photon line shapes – An overview

We shall now evaluate the lowest order approximation for \( I_{ab}(\Delta) \) (eq. (57)) using the expansions developed in the previous sections, and summarize the approximations. Both the cluster and the
perturbative expansions, to lowest order may be written in the form:

\[ I_{ab}(\Delta) = -i \int_0^\infty d\tau \exp \left[ i\Delta \tau + i(U)\tau - \frac{1}{2}(\gamma_a + \gamma_b)\tau - \int_0^\tau d\tau_1 (\tau - \tau_1) \bar{g}(\tau_1) \right] \]  

(104)

where

\[ \bar{g}(\tau) = \frac{d^2g(\tau)}{d\tau^2}. \]  

(105)

(i) The cluster expansion

To lowest order (eq. (86)) we have:

\[ g(\tau) = -n\Omega \text{Tr} \left[ \exp(iH_a^{(2)}\tau) \exp(-iH_b^{(2)}\tau) \phi_2 - 1 \right]. \]  

(106)

Here \( H_a^{(2)} \) and \( H_b^{(2)} \) include the system atom and one perturber. Denoting the eigenstates of \( H_a \) and \( H_b \) by \( |\alpha\rangle \) and \( |\beta\rangle \) respectively, we have:

\[ \bar{g}(\tau) = n\Omega \sum_{\alpha\beta} \omega_{\alpha\beta}^2 \langle \alpha|\beta\rangle \langle \beta|\alpha\rangle (\phi_2)_{\alpha\alpha} \exp(i\omega_{\alpha\beta}\tau). \]  

(107)

To lowest order in density (OCE) we set

\[ (\phi_2)_{\alpha\alpha'} \rightarrow (\phi_2)_0^{\alpha\alpha'} = P(\alpha) \delta_{\alpha\alpha'} \]  

(108)

and we get:

\[ \bar{g}(\tau) = n\Omega \sum_{\alpha\beta} \omega_{\alpha\beta}^2 P(\alpha) |\langle \alpha|\beta\rangle|^2 \exp(i\omega_{\alpha\beta}\tau). \]  

(109)

(ii) Semiclassical cluster expansion

If we wish to evaluate (106) using classical mechanics we first rewrite it as:

\[ g(\tau) = -n\Omega \left\{ \text{Tr} \exp \left[ -i \int_0^\tau d\tau_1 U(\tau_1) \right] \phi_2 - 1 \right\}. \]  

(110)

Classically we set

\[ U(\tau) = U(Q(\tau)|Q_0, P_0). \]  

(111)

which is obtained by solving Hamilton's equations using the \( H_a \) Hamiltonian and where \( Q_0 \) and \( P_0 \) are the initial values of the relative coordinates and momenta of the perturber and absorber. Also,

\[ \text{Tr} \rightarrow \int dQ_0 dP_0. \]  

(112)
We then have:

\[ g(\tau) = -n\Omega \int dQ_0 dP_0 \left\{ \exp \left[ -i \int_0^\tau d\tau_1 U^{(1)}(\tau_1) \right] - 1 \right\} g_2(Q_0) F(P_0). \]  

(113)

\( g_2(Q_0) \) is the pair distribution function (eq. (143)) and \( F(P_0) \) is the Maxwell's distribution of momenta:

\[ F(P_0) = 4\pi^{-1/2} (2\pi mkT)^{-3/2} \exp(-P_0^2/2mkT). \]  

(114)

(iii) The weak coupling limit

Taking eq. (101) to lowest order we have:

\[ \bar{g}(\tau) = \langle U(\tau) U(0) \rangle = \sum_{kk'} U_k U_{k'} \langle \hat{N}_k(\tau) \hat{N}_{-k'}(\tau) \rangle. \]  

(115)

Eq. (115) shows that \( \langle U(\tau) U(0) \rangle \) includes two and three particle correlation functions. There is one limit in which \( \langle U(\tau) U(0) \rangle \) may further be simplified. This is the Brownian particle limit in which \( s \) is much heavier than \( p \) so that we may ignore the time evolution of \( Q_s(\tau) \) in (115) and set \( Q_s(\tau) = Q_s(0) \). In this case we have:

\[ \bar{g}(\tau) = \sum_{kk'} U_k U_{k'} \langle N_{-k}(\tau) N_{-k'} \rangle. \]  

(116)

Using the definition of the dynamic structure factor [61]:

\[ \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \exp(-i\omega\tau) \langle N_{-k}(\tau) N_{-k'} \rangle = S(k, \omega) \delta_{kk'}. \]  

(117)

we have [42]:

\[ \bar{g}(\tau) = \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 S(k, \omega) \exp(i\omega\tau). \]  

(118)

Eq. (118) when substituted in eqs. (104) results in our lowest order perturbative approximation for the line shape. The relevant information which enters eq. (118) is the interaction potential \( U_k \), and \( S(k, \omega) \) which is well known from other experiments (neutron scattering, light scattering, etc.).

Eqs. (115) and (118) provide a simple connection between light scattering and line broadening experiments [61]. In the former, one directly probes \( S(k, \omega) \) since the density fluctuations are responsible for the light scattering. Eq. (118) shows that in the limit of weak line broadening (second order perturbation) then the line broadening of a heavy two-level impurity in a fluid is basically monitoring the same function \( S(k, \omega) \). We have recently used eq. (115) to study the line broadening in fluids near their critical points [62]. A universal line shape function which broadens due to the increase in density fluctuations near criticality was obtained.
(iv) The static limit

The static limit holds when the motions of the perturbers (typical time scale of $\bar{g}(\tau), \Lambda^{-1} \sim$ duration of a collision) are much slower than the observed line width $\Gamma$, i.e.

$$\frac{\Gamma}{\Lambda} \gg 1.$$  \hfill (119)

Formally we get this limit by neglecting the kinetic energy terms in the Hamiltonians $H_a$ and $H_b$ in eq. (59). We then have:

$$I_{ab}(\tau) = \langle \exp(i U \tau) \rho_a \rangle = \left\langle \prod_{p=1}^{N} [1 + \tilde{f}_{sp}(\tau)] \rho_a \right\rangle$$ \hfill (120)

where

$$\tilde{f}_{sp}(\tau) = \exp(i U^{sp} \tau) - 1.$$ \hfill (120a)

In order to express eq. (120) in terms of well known properties of the fluid let us introduce the following static correlation functions [60]:

$$n_2(r_1, r_2) = N \langle \delta(r_1 - Q_1) \delta(r_2 - Q_2) \rangle,$$

$$n_{p+1}(r_1, \ldots, r_{p+1}) = \frac{N!}{(N-p)!} \langle \delta(r_1 - Q_1) \delta(r_2 - Q_2) \cdots \delta(r_{p+1} - Q_{p+1}) \rangle.$$ \hfill (121)

Eq. (120) may then be expanded according to the number of perturbers:

$$I_{ab}(\tau) = 1 + \sum_{p=1}^{N} \frac{1}{p!} \langle (f_{s1} f_{s2} \cdots f_{sp}) n_{p+1}(r_1, r_2, \ldots, r_p, r_s) \rangle.$$ \hfill (122a)

Upon introducing the ansatz:

$$I_{ab}(\tau) = \exp\left[ \sum_{p=1}^{\infty} \frac{n^p}{p!} J_p(\tau) \right],$$ \hfill (122b)

and comparing term by term with eq. (122a), we get:

$$J_p(\tau) = \int dr_1 \cdots dr_p$$

$$\tilde{f}_{s1} \cdots \tilde{f}_{sp} \mathcal{F}_{p+1}(r_1, \ldots, r_p, r_s),$$ \hfill (123)

where $\mathcal{F}_p$ are the Ursell distribution functions [60]

$$\mathcal{F}_1 = n_1(r_1),$$ \hfill (124a)

$$\mathcal{F}_2 = n_2(r_1, r_2) - n_1(r_1) n_1(r_2).$$ \hfill (124b)
\[ \mathcal{F}_k = n_k - \sum_{t=1}^{k-1} \binom{k-1}{t} n_t(r_1, \ldots, r_t) \mathcal{F}_{k-t}(r_{t+1}, \ldots, r_k). \] (124c)

To lowest order, the line shape is given by eq. (104) where:

\[ \int_0^\tau d\tau_1 (\tau - \tau_1) g^{\text{stat}}(\tau_1) = -\Omega \int dQ \{ \exp[iU\tau] - 1 \} n_2(Q, 0). \] (125)

No trajectories need to be calculated in this limit and the line broadening is purely inhomogeneous.

(v) The Markovian (impact) limit

The Markovian limit is the important case when all the relevant correlation times of the perturbers are short compared with the observed broadening. In this limit the line shape assumes a simple almost Lorentzian form. Mathematically the impact limit is realized whenever the typical time scale of \( g(\tau) \), \( \Lambda^{-1} \) is much shorter than the observed line width \( \Gamma \), i.e.

\[ \Gamma/\Lambda \ll 1. \] (126)

(This is the opposite of the static limit.) Condition (126) implies that the short time behavior of \( \dot{g}(\tau) \) is irrelevant for our line shape. For times \( \Lambda \tau \gg 1 \) we then have

\[ \int_0^\tau d\tau_1 (\tau - \tau_1) \dot{g}(\tau_1) \equiv \tau \int_0^\tau d\tau_1 \dot{g}(\tau_1) - \int_0^\tau d\tau_1 \tau_1 \dot{g}(\tau_1) \equiv (i\Delta' + \hat{\Gamma}) \tau + \eta. \] (127)

Here

\[ -i\Delta' + \hat{\Gamma} \equiv \int_0^\infty d\tau \ddot{g}(\tau) \] (128a)

and

\[ \eta \equiv \eta' + i\eta'' = \int_0^\infty d\tau \ddot{g}(\tau), \] (128b)

where \( \ddot{g}(\tau) \) is given by any of the expressions developed previously in this section, i.e. (107), (109), (113), (115), (118) or (125). We then have:

\[ I_a^{\text{ab}}(\Delta) = \exp(-\eta') \left[ \frac{\Gamma}{(\Delta - \Delta')^2 + \Gamma^2} \cos \eta'' + \frac{\Delta' - \Delta}{(\Delta - \Delta')^2 + \Gamma^2} \sin \eta'' \right], \] (129)

where

\[ \Gamma_{ab} = \frac{1}{2}(\gamma_a + \gamma_b) + \hat{\Gamma}_{ab}. \] (130)
Typically $\eta$ is quite small [21, 22, 41] so that the line shape (129) is basically a Lorentzian with a slight asymmetry caused by the dispersive term (the second term in the brackets). In the extreme case when $|\eta| \to 0$ we have:

$$I_{ab}(\Delta) = \frac{1}{\Delta' - \Delta + i\Gamma_{ab}}$$

so that

$$I_{ab}(\Delta) = \frac{\Delta' - \Delta}{(\Delta' - \Delta)^2 + \Gamma_{ab}^2}$$

and

$$I_{ab}''(\Delta) = \frac{\Gamma_{ab}}{(\Delta - \Delta')^2 + \Gamma_{ab}^2}.$$

To summarize, in the Markovian limit the line shape is given by the parameters $I$, $\Delta'$ and $\eta''$ which are given in terms of $\tilde{g}(\tau)$.

If we use eqs. (118) we may write:

$$\hat{I} = \pi \lim_{\omega \to 0} \sum_k |U_k|^2 S(k, \omega),$$

$$\Delta' = \text{PP} \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{S(k, \omega)}{\omega},$$

$$\eta' = \text{PP} \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{\partial S(k, \omega)}{\partial \omega} \frac{1}{\omega},$$

and

$$\eta'' = \pi \lim_{\omega \to 0} \sum_k |U_k|^2 \frac{\partial S(k, \omega)}{\partial \omega}.$$

For the sake of illustration we have calculated $\tilde{g}(\tau)$ for a collinear collision model where:

$$U_a'\alpha(Q) = A_a \exp(-Q/L)$$

and

$$U_b'\beta(Q) = A_b \exp(-Q/L).$$

The model is characterized by two parameters, the range of the potential $L$ and a dimensionless
coupling parameter \( c \):

\[
c \equiv \frac{A_b - A_a}{A_a}.
\]  

(134)

We have calculated the dimensionless single particle line broadening function [63]:

\[
J(\omega) = \frac{1}{2\pi f} \int_{-\infty}^{\infty} d\tau \bar{g}(\tau) \exp(-i\omega \tau)
\]  

(135)

where \( f \) is the frequency of binary collinear collisions, using the quantum expression (eq. (109)) and the semiclassical expression (eq. (113)). We then calculated the line shape function (eq. (104)). In figs. 4 and 5 we present the results of our calculations [63] for a two-level absorber in liquid nitrogen \((T = 77^\circ K)\), and in liquid helium \((T = 4.2^\circ K)\). For each case we varied the magnitude of the interaction responsible

![Fig. 4. Quantum (eq. (109)) and semiclassical (eq. (113)) calculations for a two level absorber in N\(_2\), for several values of the interaction strength parameter \( c \) (eq. (134)) [63]. The temperature \( T = 77^\circ K \), the absorber-perturber reduced mass \( \mu = 14 \) amu, the range of the interaction potential \( L = 0.2 \) \AA and the frequency of collinear collisions \( f = 0.8 \times 10^{13} \) Hz. (a) The dimensionless single perturber spectral function \( J(\omega) \) (eq. (135)). (b) The absorption line shape (eqs. (60) and (104)) \( \sigma_{\text{ab}}(\Delta) = (1/\pi)f_{\text{ab}}(\Delta) \).]
Fig. 5. Quantum (eq. (109)) and semiclassical (eq. (113)) calculations for a two level absorber in He, for several values of interaction strength parameters $c$ (eq. (134)) [63]. The temperature $T = 4.2$°K, the absorber-perturbers reduced mass $\mu = 3.5$ amu, the range of the interaction potential $L = 0.2$ Å, and the frequency of collinear collisions $f = 0.8 \times 10^{13}$ Hz. (a) The dimensionless single perturber spectral function $J(\omega)$ (eq. (135)). (b) The absorption line shape (eqs. (60) and (104)) $\sigma^{ab}(\Delta) = (1/\pi) I^{ab}(\Delta)$.

for the line broadening by varying $c$ (eq. (134)). The various parameters were chosen as follows [64]:
The two-level absorber was assumed to have the mass of N$_2$ ($M_1 = 28$), $L$ was taken to be 0.2 Å and the
frequency $f$ of binary collinear collisions was given the typical value of $0.8 \times 10^{13}$ Hz. Figure 4a shows the
quantum mechanical and classical $J(\omega)$ for the two-level absorber in N$_2$ whereas fig. 4b gives the
corresponding line shapes $\sigma^{ab}(\Delta) = (1/\pi) I^{ab}(\Delta)$. Figure 5 contains the same quantities for the other
solvent (He).

The following points should now be made:
1. The duration of collision $\Lambda^{-1}$ is given by the inverse spectral width of $J(\omega)$ which is of the order of
0.01 psec in all cases. By decreasing the line broadening interaction $c$ we are decreasing the observed
line width and, when $c$ is small enough, the resulting line is narrower than the duration of collision $\Lambda^{-1}$
(Markovian limit) (eq. (126)). Our calculations for $c = 0.65 \times 10^{-2}$ are in the Markovian limit and as $c$
increases we tend towards the static limit, although the condition $f^{\tau_c} \gg 1$ is never realized for our
parameters so that we do not reach the static limit. In the strong coupling case ($c = 4$) the line is broad
and asymmetric and does not tend towards a Gaussian as implied by simple stochastic models [20].
2. The line shapes all exhibit a blue shift. This arises as we are using a purely repulsive potential and took \( A_b > A_a \) so that \( U \) is always positive. By including an attractive part in the potential we may get a red shift, as is usually the case for solvent shifts.

3. The quantum effects on \( J(\omega) \) and \( \sigma_{ab}(\Delta) \) increase dramatically as we go from \( \text{N}_2 \) to He since the mass of the perturber becomes smaller and the temperature decreases. \( \text{N}_2 \) is almost classical and the difference between the quantum and classical results is small. For He the classical calculations of \( J(\omega) \) are very different from the quantum ones. Thus when studying line broadening in cryogenic liquids, it is necessary to perform quantum Franck–Condon type calculations of the line broadening.

4. The microscopic information content of \( \sigma_{ab}(\Delta) \) is very small in the Markovian limit (small \( c \)), since then \( \sigma_{ab}(\Delta) \) depends essentially on \( J(0) \) (eq. (128a)) and is insensitive to the details of \( J(\omega) \). Only for the larger values of \( c \), \( \sigma_{ab}(\Delta) \) contains a significant microscopic information.

(vi) A stochastic model – The Gaussian random modulation

This simple two-parameter model developed by Kubo [20], was applied with remarkable success to many systems. The model assumes that the frequency \( \omega_{ba} \) undergoes a stationary Gaussian process resulting in:

\[
\tilde{g}(\tau) = \delta^2 \exp(-\Lambda \tau) \tag{136a}
\]

so that

\[
\int_0^\tau d\tau_1 (\tau - \tau_1) \tilde{g}(\tau_1) = \frac{\delta^2}{\Lambda^2} \left[ \exp(-\Lambda \tau) - 1 + \Lambda \tau \right]. \tag{136b}
\]

Here \( \delta \) is a measure of the coupling strength responsible for the line broadening (the amplitude of the frequency fluctuations) and \( \Lambda^{-1} \) is a correlation time which measures the typical time scale of \( \tilde{g}(\tau) \) (i.e. the duration of a collision). The nature of the line shape function \( I''_{ab}(\Delta) \) is dominated by the dimensionless parameter \( \kappa \),

\[
\kappa \equiv \Lambda/\delta. \tag{136c}
\]

When \( \kappa \gg 1 \) we are in the Markovian (impact) limit,

\[
\exp\left[ - \int_0^\tau d\tau_1 (\tau - \tau_1) \tilde{g}(\tau_1) \right] \equiv \exp\left( -\frac{\delta^2}{\Lambda} \tau \right), \quad (\kappa \gg 1) \tag{137}
\]

and

\[
I''_{ab}(\Delta) = \Gamma_{ab}/(\Delta^2 + \Gamma_{ab}^2), \tag{137a}
\]

where \( \gamma = \gamma_a + \gamma_b \) and

\[
\Gamma_{ab} = \frac{1}{2} \gamma + \delta^2 / \Lambda \tag{137b}
\]
Whereas when \( \kappa \ll 1 \) we are in the static limit,\n
\[
\exp\left[-\int_0^\tau d\tau_1 (\tau - \tau_1) \tilde{g}(\tau_1) \right] = \exp\left(-\frac{1}{2} \delta^2 \tau^2 \right), \quad (\kappa \ll 1)
\]

and the line shape assumes the Voigt profile\n
\[
I_{ab}(\Delta) = \frac{1}{\sqrt{8\pi\cdot\delta}} \int d\Delta' \frac{\gamma}{(\Delta - \Delta')^2 + \frac{1}{4} \gamma^2} \exp\left(-\frac{\Delta'^2}{2\delta^2}\right)
\]

which when \( \gamma \ll \delta \), becomes a Gaussian:\n
\[
I_{ab}(\Delta) = \sqrt{\frac{\pi}{2\delta^2}} \exp\left(-\frac{\Delta^2}{2\delta^2}\right).
\]

In fig. 6 we display a few calculations of the line shape function (eq. (104) together with eq. (136)). This line shape will be extensively used later in our numerical calculations.

In concluding this section we shall make a few comments regarding the moments of the line shape function (104). The spectral moments of the line shape function \( I''_{ab}(\Delta) \) provide a convenient means for evaluating the accuracy of various approximations and are widely used in comparing experimental and theoretical results. The \( k \)th moment is defined as:

\[
M_k = \frac{1}{\pi} \int_{-\infty}^{\infty} d\Delta I''_{ab}(\Delta) \Delta^k, \quad k = 0, 1, \ldots
\]

We shall now write explicit expressions for the various moments. Using eqs. (101) and (103) and well
known properties of Fourier transforms:

\[ M_0 = 1, \]
\[ M_1 = 0, \]
\[ M_k = \langle U^k \rangle, \quad k \geq 2, \]

we now introduce the definition of another type of static correlation function of the fluid [60]

\[ g_{p+1}(r_1, r_2, \ldots r_p) = \Omega \frac{n_{p+1}(r_1, r_2, \ldots r_p)}{n^p}; \]

note that \[ g_{p+1} \] are dimensionless.

Making use of the definition (143) we have:

\[ M_2 = n \int dr \, U^2(r) \, g_2(r) + n^2 \int dr_1 \, dr_2 \, U(r_1) \, U(r_2) \, g_3(r_1, r_2). \]

In general \[ M_p \] will depend on all the \( q \)-body static correlation functions \( g_q \) with \( q \leq p + 1 \) (\( p \) perturbers plus the absorber atom).

5. Two-photon processes

The simplest multiphoton process is a two-photon process in a three-level system [65–74]. We shall consider here two modes of the radiation field (with frequencies \( \omega_L \) and \( \omega_s \)), and treat in a unified way a Raman process (fig. 7a) and a two-photon absorption (TPA) (fig. 7b). In a Raman process a photon is absorbed from the \( \omega_L \) mode and an \( \omega_s \) photon is being scattered. The relevant eigenvectors of \( \hat{H}_s + \hat{H}_R \) within the rotating wave approximation (the "system" states) are therefore:

\[ |a\rangle = |\bar{a}, n_L, 0\rangle \]
\[ |b\rangle = |\bar{b}, n_L - 1, 0\rangle \]
\[ |c\rangle = |\bar{c}, n_L - 1, 1\rangle \]

with the eigenvalues:

\[ E_a = \varepsilon_a + \omega_L, \]
\[ E_b = \varepsilon_b, \]
Fig. 7. Two-photon processes in a three level system ([a], [b] and [c]) interacting with two modes of the radiation field with frequencies $\omega_L$ and $\omega_s$. The corresponding frequency detunings are denoted by $\Delta_L$ and $\Delta_s$. (a) A resonance Raman process. (b) Two-photon absorption.

and

$$E_c = \varepsilon_c + \omega_s.$$  \hspace{1cm} (146c)

In a TPA experiment one photon is being absorbed from each of the modes. The relevant "system" states are therefore:

$$|a\rangle = |a, n_L, n_s\rangle,$$  \hspace{1cm} (147a)

$$|b\rangle = |b, n_L - 1, n_s\rangle,$$  \hspace{1cm} (147b)

$$|c\rangle = |c, n_L - 1, n_s - 1\rangle.$$  \hspace{1cm} (147c)

with eigenvalues:

$$E_a = \varepsilon_a + \omega_L + \omega_s,$$  \hspace{1cm} (148a)

$$E_b = \varepsilon_b + \omega_s,$$  \hspace{1cm} (148b)

and

$$E_c = \varepsilon_c.$$  \hspace{1cm} (148c)

We shall define the detuning parameters (fig. 7)

$$\Delta_L = E_a - E_b = \omega_L - \omega_{ba}$$  \hspace{1cm} (149a)

$$\Delta_s = E_c - E_b = \left\{ \begin{array}{ll} \omega_s - \omega_{bc} & \text{(Raman)} \\ \omega_{cb} - \omega_s & \text{(TPA)} \end{array} \right.$$  \hspace{1cm} (149b)
The different definition of $\Delta_s$ (eq. (149b)) is the only difference between the theories of Raman and TPA. From now on we shall consider Raman spectra but all the results of this section apply to TPA as well.

For a two-photon process we will evaluate $\mathcal{F}$ (eqs. (36) and (37)) to fourth order and the corresponding line shape function is given by:

$$
\hat{I}(\Delta_L, \Delta_s) = -i \langle \langle cc | \mathcal{F}^{(4)}(\omega = 0) | \rho_a \rangle \rangle = (-i)^4 \int_0^\infty dt_1 \int_0^t dt_2 \int_0^{t_2} dt_3

\times \langle \langle cc | \mathcal{V}(t_1) \mathcal{G}_s(t_1 - t_2) \mathcal{V}(t_2) \mathcal{G}_s(t_2 - t_3) \mathcal{V}(t_3) \mathcal{G}_s(t_3) \mathcal{V}(0) | \rho_a \rangle \rangle .
$$

(150)

A simple inspection of fig. 8 shows that there are three different pathways (plus their complex conjugates) which contribute to $\hat{I}(\Delta_L, \Delta_s)$. We thus define:

$$
\langle \langle cc | \mathcal{V}(t_1) \cdots \mathcal{V}(0) | \rho_a \rangle \rangle = I + II + III + c.c.
$$

(151)

where

$$
I = \exp[-i \Delta_s(t_1 - t_2) - \frac{1}{2}(\gamma_a + \gamma_b)(t_1 - t_2) - \gamma_b(t_2 - t_3) - i\Delta_L t_3 - \frac{1}{2}(\gamma_a + \gamma_b)t_3]

\times \text{Tr}_{B}(\langle \langle cc | \mathcal{V}(t_1) | bc \rangle \rangle_s \langle \langle cb | \mathcal{V}(t_2) | bb \rangle \rangle_s \langle \langle bb | \mathcal{V}(t_3) | ab \rangle \rangle_s \langle \langle ab | \mathcal{V}(0) | aa \rangle \rangle_s | \rho_a \rangle
$$

(152a)

$$
II = \exp[-i \Delta_s(t_1 - t_2) - \frac{1}{2}(\gamma_b + \gamma_c)(t_1 - t_2) - \gamma_b(t_2 - t_3) - i\Delta_L t_3 - \frac{1}{2}(\gamma_a + \gamma_b)t_3]

\times \text{Tr}_{B}(\langle \langle cc | \mathcal{V}(t_1) | bc \rangle \rangle_s \langle \langle bc | \mathcal{V}(t_2) | bb \rangle \rangle_s \langle \langle bb | \mathcal{V}(t_3) | ab \rangle \rangle_s \langle \langle ab | \mathcal{V}(0) | aa \rangle \rangle_s | \rho_a \rangle
$$

(152b)

$$
III = \exp[-i \Delta_s(t_1 - t_2) - \frac{1}{2}(\gamma_b + \gamma_c)(t_1 - t_2) - i(\Delta_s - \Delta_L) (t_3 - t_2) - \frac{1}{2}(\gamma_a + \gamma_c)(t_3 - t_2) - i\Delta_L t_3

- \frac{1}{2}(\gamma_a + \gamma_b)t_3]

\times \text{Tr}_{B}(\langle \langle cc | \mathcal{V}(t_1) | bc \rangle \rangle_s \langle \langle bc | \mathcal{V}(t_2) | ac \rangle \rangle_s \langle \langle ac | \mathcal{V}(t_3) | ab \rangle \rangle_s \langle \langle ab | \mathcal{V}(0) | aa \rangle \rangle_s | \rho_a \rangle .
$$

(152c)

Fig. 8. The pathways in Liouville space which contribute to two-photon spectra. There are three pathways (plus three complex conjugate pathways) which lead from $|aa\rangle$ to $|cc\rangle$ in fourth order. These correspond to the terms $I$, $II$ and $III$ in eq. (152).
The subscript s signifies that the trace in each matrix element is taken over the system only and the entire product should then be averaged over the bath via the operation $\text{Tr}_B(\cdots \rho_a)$. At this stage we wish to evaluate the matrix elements of eqs. (152). To that end we recall that each time the left (right) index changes in the matrix element $\langle \langle V | V | \rangle \rangle$ it means that the operator $V$ acted from left (right). If we focus on pathway (I) we note that $V(0)$ and $V(t_1)$ operate from right whereas $V(t_2)$ and $V(t_3)$ operate from the left. We thus have:

$$\text{(I)} = \exp[\cdots] \text{Tr}_B [V_{cb}(t_2) V_{ba}(t_3) \rho_a(-\infty) V_{ab}(0) V_{bc}(t_1)] = \exp[\cdots] \langle V_{ab}(0) V_{bc}(t_1) V_{cb}(t_2) V_{ba}(t_3) \rangle \cdot \quad (153a)$$

In the second equality in (153a) we have used the cyclic permutation invariance of the trace. Similarly we have for pathways (II) and (III):

$$\text{(II)} = \exp[\cdots] \text{Tr}_B [V_{cb}(t_1) V_{ba}(t_3) \rho_a(-\infty) V_{ab}(0) V_{bc}(t_2)]$$

$$= \exp[\cdots] \langle V_{ab}(0) V_{bc}(t_2) V_{cb}(t_1) V_{ba}(t_3) \rangle \quad (153b)$$

$$\text{(III)} = \exp[\cdots] \text{Tr}_B [V_{cb}(t_1) V_{ba}(t_2) \rho_a(-\infty) V_{ab}(0) V_{bc}(t_3)]$$

$$= \exp[\cdots] \langle V_{ab}(0) V_{bc}(t_2) V_{cb}(t_1) V_{ba}(t_3) \rangle \quad (153c)$$

where the $\exp[\cdots]$ factors are the same as in eqs. (152). Eqs. (153) show that the various pathways result in essentially the same four point correlation function with a simple permutation of the time arguments. Using eqs. (150)–(153) we thus get:

$$\hat{f} = \mu_L^2 \mu_s^2 \int_0^\infty dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{ \phi(t_1, t_2, t_3) F(t_1, t_2, t_3)$$

$$+ \phi(t_2, t_1, t_3) F(t_2, t_1, t_3) + \phi(t_3, t_1, t_2) F(t_3, t_1, t_2) \} + \text{c.c.} \ , \quad (154)$$

where

$$\mu_L = |\mu_{ab}|, \quad \mu_s = |\mu_{bc}|,$$

$$\phi(t_1, t_2, t_3) = \exp[-i \Delta t_1 t_3 - i \Delta t_3 t_2 - \frac{1}{2} \gamma_a t_1 + t_2 - t_3 - \frac{1}{2} \gamma_b t_1 - t_2] \ , \quad (155)$$

$$\mu_L^2 \mu_s^2 F(t_1, t_2, t_3) \equiv \langle V_{ab}(0) V_{bc}(t_1) V_{cb}(t_2) V_{ba}(t_3) \rangle$$

$$= \text{Tr}_B [V_{ab}(0) V_{bc}(t_1) V_{cb}(t_2) V_{ba}(t_3) \rho_a] \ , \quad (156)$$

$$A(\tau) \equiv \exp(i H_1 \tau) A \exp(-i H_1 \tau) \ . \quad (157)$$

The significance of eq. (154) is clear. As is obvious from fig. 8, the various pathways are formed by the successive application of two perturbations from left and two from the right. The various pathways simply differ in the order in time in which these four perturbations are applied. Eq. (154) is nothing but a sum of all the possible sequences in time which lead from $|aa\rangle$ to $|cc\rangle$. Figure 8 is therefore a very compact bookkeeping device and is equivalent to the Feynman diagrams used in other methods [9].
In concluding this subsection we note that eqs. (154)—(156) express the two-photon cross section in terms of the four time correlation function $F(t_1, t_2, t_3)$. Upon substitution of eq. (1c) in eq. (156) we finally get:

$$F(t_1, t_2, t_3) = \langle \exp(iH_b t_1) \exp(-iH_c t_1) \exp(iH_b t_2) \exp(-iH_c t_2) \exp(iH_b t_3) \exp(-iH_a t_3) \rangle.$$  \hfill (158)

The rest of this section will be devoted to various techniques for the evaluation of (158).

5.1. The dressed cluster expansion

The dressed cluster expansion for the four-point correlation function $F(t_1, t_2, t_3)$ proceeds along the same lines developed in section 4 for the two-point correlation function. The basic goal is, as before, to use exact static correlations plus few body dynamics towards the evaluation of $F$. In analogy with eq. (63) we define:

$$f_{bc}(t_1) = \exp(iH_b t_1) \exp(-iH_c t_1) - 1,$$  \hfill (159a)

$$f_{cb}(t_2) = \exp(iH_c t_2) \exp(-iH_b t_2) - 1,$$  \hfill (159b)

and

$$f_{ba}(t_3) = \exp(iH_b t_3) \exp(-iH_a t_3) - 1,$$  \hfill (159c)

so that

$$F(t_1, t_2, t_3) = \langle [1 + f_{bc}(t_1)] [1 + f_{cb}(t_2)] [1 + f_{ba}(t_3)] \rangle.$$  \hfill (160)

The operators $f$ have the desirable property that they vanish when all atoms are far apart. In complete analogy with eq. (73) we may now write:

$$1 + f_{bc}(\tau) = \hat{T}_{bc} \prod_{j,k} [1 + f_{bc}^{jk}(\tau)]$$  \hfill (161a)

$$1 + f_{cb}(\tau) = \hat{T}_{cb} \prod_{l,m} [1 + f_{cb}^{lm}(\tau)]$$  \hfill (161b)

$$1 + f_{ba}(\tau) = \hat{T}_{ba} \prod_{u,v} [1 + f_{ba}^{uv}(\tau)]$$  \hfill (161c)

where $j, k, l, m, u, v$ run over all particles (absorber plus perturbers).

We thus have:

$$F(t_1, t_2, t_3) = \hat{T}_{bc} \hat{T}_{cb} \hat{T}_{ba} \prod_{j,k} \prod_{l,m} \prod_{u,v} \langle [1 + f_{bc}^{jk}(t_1)] [1 + f_{cb}^{lm}(t_2)] [1 + f_{ba}^{uv}(t_3)] \rangle.$$  \hfill (162)

Eq. (162) (analogous to eq. (73)) is a key step in the cluster expansion and it allows us to rearrange the products in the r.h.s. at will without having to worry about commutators since the $T$ operators in front
will finally take care of the appropriate time ordering. The dressed cluster expansion now proceeds as in section 4.1. We first consider a system consisting of the absorber plus \( p \) "dressed" perturbers in a volume \( \Omega \). The corresponding \( F \) will be denoted \( F_p(t_1, t_2, t_3) \). For \( p = 1 \) (absorber plus a single perturber) we have, using eq. (162):

\[
F_1(t_1, t_2, t_3) = 1 + \frac{1}{\Omega} \chi_1(t_1, t_2, t_3)
\]

where

\[
\chi_1(t_1, t_2, t_3) = \Omega \left[ \langle f_{bc}^{11}(t_1) \phi_2(X_0, X_1) \rangle + \langle f_{cb}^{11}(t_2) \phi_2(X_0, X_1) \rangle + \langle f_{ba}^{11}(t_3) \phi_2(X_0, X_1) \rangle 
+ \langle f_{bc}^{11}(t_1) f_{cb}^{11}(t_2) \phi_2(X_0, X_1) \rangle 
+ \langle f_{cb}^{11}(t_1) f_{ba}^{11}(t_3) \phi_2(X_0, X_1) \rangle 
+ \langle f_{cb}^{11}(t_1) f_{ba}^{11}(t_3) \phi_2(X_0, X_1) \rangle \right]. \tag{164}
\]

As in section 4.1, the "dressing" arises since we are using the reduced two-particle static distribution function, \( \phi_2 \) (eq. (74)) rather than \( \phi_0 \) (eq. (76)) which correspond to a cluster of two particles. Since all factors \( f \) vanish unless \((Q_0 - Q)\) is microscopically small, then each \( \langle \cdots \rangle \) factor is \( O(1/\Omega) \) so that \( \chi_1 \) is \( O(1) \). (This is the reason for the \( \Omega \) factor in eq. (164).) Turning now to the two-perturber spectrum \( (p = 2) \) we have in a similar manner:

\[
F_2(t_1, t_2, t_3) = 1 + \frac{2}{\Omega} \chi_1(t_1, t_2, t_3) + \frac{1}{\Omega^2} \chi_2(t_1, t_2, t_3). \tag{165}
\]

\( \chi_2 \) contains all the terms where the absorber and the two perturbers are close and the static distribution function which enters is \( \phi_3(X_0, X_1, X_2) \). For a general number of perturbers we have, as a natural generalization of eqs. (79) and (81):

\[
F_p(t_1, t_2, t_3) = 1 + \sum_{q=1}^{p} \frac{1}{\Omega^q} \binom{p}{q} \chi_q(t_1, t_2, t_3) \tag{166}
\]

where \( \chi_q \) depends on the reduced \( q + 1 \) particles static distribution function \( \phi_{q+1}(x_0, x_1, \ldots, x_q) \).

In complete analogy with eqs. (82) we now have:

\[
\chi_1(t_1, t_2, t_3) = \Omega [F_1(t_1, t_2, t_3) - 1] \tag{167a}
\]

\[
\chi_2(t_1, t_2, t_3) = \Omega^2 [F_2(t_1, t_2, t_3) - 2F_1(t_1, t_2, t_3) + 1] \tag{167b}
\]

etc.

In the thermodynamic limit, in analogy with eq. (85) we get:

\[
F(t_1, t_2, t_3) = 1 + \sum_{q=1}^{\infty} \frac{n^q}{q^q} \chi_q(t_1, t_2, t_3). \tag{168}
\]

The final step in our expansion will now be made. The expansion (168) will be resummed by introducing
the ansatz:

\[ F(t_1, t_2, t_3) = \exp \left[ \sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(t_1, t_2, t_3) \right]. \] (169)

\( J_q \) may be obtained by comparing the expansions (168) and (169) term by term, i.e.

\[ \sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(t_1, t_2, t_3) = \log \left[ 1 + \sum_{q=1}^{\infty} \frac{n^q}{q!} \chi_q(t_1, t_2, t_3) \right]. \] (170)

Using eq. (170) \( J_q \) will be expressed in terms of \( \chi_{q'} \) where \( q' \leq q \); i.e.

\[ J_1(t_1, t_2, t_3) = \chi_1(t_1, t_2, t_3) \] (171a)

\[ J_2(t_1, t_2, t_3) = \chi_2(t_1, t_2, t_3) - \chi_1^2(t_1, t_2, t_3) \] (171b)

e tc.

Eqs. (169) and (171) are analogous to eqs. (86) and (88).

In concluding this section we note the following:

1. Eq. (169) together with (171) is our final result for the cluster expansion of two photon processes. We may actually use two different cluster expansions: the DCE and the OCE which use \( \phi_{p+1} \) (eq. (74)) or \( \phi_{p+1}^0 \) (eq. (76)) respectively as the static distribution functions in the calculations of the \( \chi_p \)'s. A low order DCE includes many-body static correlations of the fluid which appear in the OCE only in higher orders.

2. \( J_p \) is given in terms of the \( p \)-perturbers functions \( F_p \) (eq. (166)). The \( p \)th order is obtained by calculating the spectrum of our absorber plus \( p \)-perturbers eq. (166) using the static distribution functions (74) or (76). We then get \( \chi_1, \ldots, \chi_p \), \( J_1, \ldots, J_p \) are obtained from \( \chi_1, \ldots, \chi_p \) using eqs. (171).

3. The exactly solvable Anderson–Talman model is defined by taking \( U^{\text{pert}} = 0 \) in eq. (3), i.e. we assume that the bath atoms do not interact with each other but only interact with the absorber. For this model it is easy to show that \( J_q(\tau) \) with \( q \geq 2 \) vanish identically and we have the exact result:

\[ F^{(\text{AT})}(t_1, t_2, t_3) = \exp[nJ_1(t_1, t_2, t_3)]. \] (172)

Eq. (172) is analogous to eq. (89).

5.2. The perturbative expansion

The cluster expansion expresses the two-photon cross section in terms of static distribution functions of the fluid (\( \phi_{p+1} \) or \( \phi_{p+1}^0 \)) and the dynamics of a few particles (single perturber, two perturbers, etc.). An alternative type of expansion is perturbative in the interaction responsible for the line broadening, which enables us to use standard dynamical correlation functions as our input information for the line broadening. The perturbative expansion is not unique and there are various ways for carrying it out depending on the choice of a zero order Hamiltonian (\( H_a, H_b \) or \( H_c \)) [75, 44]. In this section we choose \( H_b \) as our zero order Hamiltonian and write:
\[ \exp(iH_{A}t_{1}) \exp(-iH_{B}t_{1}) = \exp\left(-i \int_{0}^{t_{1}} d\tau \ U_{cb}(\tau)\right) \]  
\[ \exp(iH_{A}t_{2}) \exp(-iH_{B}t_{2}) = \exp\left(-i \int_{0}^{t_{2}} d\tau \ U_{cb}(\tau)\right) \]  
\[ \exp(iH_{A}t_{3}) \exp(-iH_{B}t_{3}) = \exp\left(-i \int_{0}^{t_{3}} d\tau \ U_{ab}(\tau)\right) \]

where

\[ U_{cb}(\tau) = \exp(iH_{b}\tau) \left( U_{c} - U_{b} \right) \exp(-iH_{b}\tau) \]  
\[ U_{ab}(\tau) = \exp(iH_{b}\tau) \left( U_{a} - U_{b} \right) \exp(-iH_{b}\tau). \]

Upon substituting eqs. (173) in eq. (158) we get:

\[ F(t_{1}, t_{2}, t_{3}) = \left( \exp\left(-i \int_{0}^{t_{1}} d\tau \ U_{cb}(\tau)\right) \exp\left(i \int_{0}^{t_{2}} d\tau \ U_{cb}(\tau)\right) \exp\left(-i \int_{0}^{t_{3}} d\tau \ U_{ab}(\tau)\right) \right). \]  

The final step in the perturbative expansion is achieved by introducing the ansatz (see eq. (101)):

\[ F(t_{1}, t_{2}, t_{3}) = \exp\left[ \sum_{q=1}^{\infty} \frac{(-i\lambda)^{q}}{q!} K_{q}(t_{1}, t_{2}, t_{3}) \right]. \]

The various terms \( K_{q} \) may be obtained by expanding equations (175) and (176) in a power series in \( \lambda \) and comparing term by term. We thus get:

\[ K_{1}(t_{1}, t_{2}, t_{3}) = \int_{0}^{t_{1}} d\tau \langle U_{cb}(\tau) \rangle - \int_{0}^{t_{2}} d\tau \langle U_{cb}(\tau) \rangle + \int_{0}^{t_{3}} d\tau \langle U_{ab}(\tau) \rangle, \quad \text{etc.} \]

More explicit expressions will be presented in the next section where we shall carry out this expansion in a slightly different way.

5.3. Practical methods for the calculation of two-photon line shapes – An overview

We shall now summarize our results for two-photon processes and consider various practical ways for the evaluation of \( \tilde{I}(\Delta t_{A}, \Delta s) \). As is evident from eq. (154), the problem boils down to the evaluation of \( F(t_{1}, t_{2}, t_{3}) \) (eq. (158)).
(i) **First order cluster expansion**

Using eq. (169) to lowest order, we have:

\[ F(t_1, t_2, t_3) = \exp[n \chi_1(t_1, t_2, t_3)] . \]

(178)

In order to evaluate \( \chi_1(t_1, t_2, t_3) \) (eq. (164)) we need consider one absorber plus a single perturber. Upon eliminating the center of mass motion, \( H_a, H_b \) and \( H_c \) become single particle Hamiltonians with eigenstates \(|aa\), \(|b\beta\) and \(|c\gamma\) and eigenvalues \( E_{aa}, E_{b\beta} \) and \( E_{c\gamma} \) respectively, i.e.

\[ H_a|aa\rangle = E_{aa}|aa\rangle \]

(179a)

\[ H_b|b\beta\rangle = E_{b\beta}|b\beta\rangle \]

(179b)

\[ H_c|c\gamma\rangle = E_{c\gamma}|c\gamma\rangle . \]

(179c)

Eqs. (159) together with (179) result in:

\[ f_{bc}(t_1) = \sum_{\beta \gamma} |b\beta\rangle \langle b\beta|c\gamma\rangle \exp(i\omega_{\beta\gamma}t_1) - 1 \langle c\gamma| , \]

(180a)

\[ f_{cb}(t_2) = \sum_{\beta \gamma} |c\gamma\rangle \langle c\gamma|b\beta\rangle \exp(i\omega_{\beta\gamma}t_2) - 1 \langle b\beta| , \]

(180b)

\[ f_{ba}(t_3) = \sum_{\alpha \beta} |b\beta\rangle \langle b\beta|a\alpha\rangle \exp(i\omega_{\beta\alpha}t_3) - 1 \langle a\alpha| , \]

(180c)

\[ \phi_2^0 = \sum_{\alpha} |a\alpha\rangle P(\alpha) \langle a\alpha| . \]

(181)

By inspecting eq. (164) we note that \( \chi_1 \) consists of three terms containing a single \( f \) factor, three terms with two \( f \) factors and one term with three \( f \) factors. We shall denote these terms \( W_1, W_2 \) and \( W_3 \) respectively. Using eqs. (164), (180) and (181) we finally get:

\[ \chi_1(t_1, t_2, t_3) \equiv W_1 + W_2 + W_3 \]

(182)

where

\[ W_1 = \Omega \sum_{\alpha \beta \gamma} P(\alpha) \langle a\alpha|b\beta\rangle \langle b\beta|c\gamma\rangle \langle c\gamma|a\alpha\rangle \left[ \exp(i\omega_{\beta\gamma}t_1) - 1 \right] \]

+ \( \Omega \sum_{\alpha \beta \gamma} P(\alpha) \langle a\alpha|c\gamma\rangle \langle c\gamma|b\beta\rangle \langle b\beta|a\alpha\rangle \left[ \exp(i\omega_{\beta\gamma}t_2) - 1 \right] \]

+ \( \Omega \sum_{\alpha \beta} P(\alpha) |a\alpha|b\beta|^2 \left[ \exp(i\omega_{\beta\alpha}t_3) - 1 \right] \)

(182a)
\[ W_2 = \Omega \sum_{\alpha \beta \gamma} P(\alpha) \langle \alpha \alpha | \beta \beta \rangle \langle \beta \gamma | \beta \gamma \rangle \langle \beta \beta | \alpha \alpha \rangle \]
\[ \times \{ \exp(i\omega_{\beta t_1}) - 1 \} \{ \exp(i\omega_{\gamma t_2}) - 1 \} \{ \exp(i\omega_{\alpha t_3}) - 1 \} \]
\[ + \Omega \sum_{\alpha \beta \gamma} P(\alpha) \langle \alpha \alpha | \gamma \beta \rangle \langle \gamma \beta | \beta \beta \rangle \langle \beta \beta | \alpha \alpha \rangle \{ \exp(i\omega_{\beta t_2}) - 1 \} \{ \exp(i\omega_{\alpha t_3}) - 1 \} \]  
(182b)

\[ W_3 = \Omega \sum_{\alpha \beta \gamma} P(\alpha) \langle \alpha \alpha | \beta \beta \rangle \langle \beta \gamma | \beta \gamma \rangle \langle \beta \beta | \alpha \alpha \rangle \]
\[ \times \{ \exp(i\omega_{\beta t_1}) - 1 \} \{ \exp(i\omega_{\gamma t_2}) - 1 \} \{ \exp(i\omega_{\alpha t_3}) - 1 \} \]  
(182c)

Eqs. (182) clearly define the precise information content of two-photon spectra in the binary collision approximation. Together with eqs. (178) and (154) they yield a closed expression for the spectrum. We note that a two-photon cross section depends on various multitime quantities which do not appear in the theory of single photon processes. Thus the three line shape functions \( I'_{\alpha}(\Delta), I'_{\beta}(\Delta) \) and \( I'_{\gamma}(\Delta) \) do not contain all the information that enters eqs. (182). Eq. (178) together with (182) is a generalization of a recent study of the same model system [74] in which several perturbative assumptions were made, and is the exact expression to lowest order in density \( n \).

(ii) The semiclassical cluster expansion

Eq. (175) can also be used to develop a semiclassical non-perturbative approximation for \( F \). It should be noted that \( F(t_1, t_2, t_3) \) is not an analytic function of \( \hbar \) so that its semiclassical limit is not unique [75]. In eq. (175), we chose \( H_B \) as our zero-order Hamiltonian and therefore if we use it as the starting point for our expansion we get an approximation that involves the calculation of classical trajectories using the \( U_B \) potential. Alternatively we could have used \( H_a \) or \( H_c \) to be our zero-order Hamiltonian and the final semiclassical result will be different. A detailed analysis of this non-uniqueness was recently made [75]. Coming back to eq. (175), the semiclassical limit is achieved using the following substitutions (see section 4.3):

\[ U_{\nu \mu}(\tau) \rightarrow U_{\nu \mu}(Q(\tau) | P_0, Q_0), \quad \nu \mu = cb, ba \]  
(183a)

\[ \exp_{\pm} \rightarrow \exp, \]  
(183b)

and

\[ \text{Tr}_B = \int dP_0 dQ_0 \]  
(183c)

where \( U_{\nu \mu}(Q(\tau) | P_0, Q_0) \) is the value of \( U_{\nu \mu}(Q) \) at \( Q = Q(\tau) \). \( Q(\tau) \) is obtained by solving a classical trajectory on the \( H_B \) Hamiltonian with the initial conditions \( Q = Q_0 \) and \( P = P_0 \). Upon substitution of eqs. (183) in eq. (175) we finally get:

\[ \chi_1(t_1, t_2, t_3) = \Omega \left\{ \int dP_0 dQ_0 \exp \left[ -i \int_0^{\tau_1} d\tau U_{cb}(Q(\tau) | P_0, Q_0) + i \int_0^{\tau_2} d\tau U_{cb}(Q(\tau) | P_0, Q_0) \right] \right\} \]
\[ - i \int_0^{\tau_1} d\tau U_{ba}(Q(\tau) | P_0, Q_0) \]  
(184)
(iii) The static limit

The static limit is obtained by neglecting the kinetic energy terms in the Hamiltonians $H_a$, $H_b$, $H_c$ in eq. (175). We then get an expansion analogous to eqs. (122)–(124). To lowest order we have:

$$\chi_1(t_1, t_2, t_3) = \Omega \left\{ \int \int dP_0 dQ_0 \exp \left[ i U_{ca}(Q_0) (t_2 - t_1) - i U_{ba}(Q_0) t_3 \right] \phi_2(P_0, Q_0) - 1 \right\}. \quad (185)$$

The evaluation of $\chi_1$ involves thus merely a static average over configurations and no trajectories need to be calculated in this case.

(iv) The weak coupling limit

The weak coupling limit may be obtained by expanding $K(t_1, t_2, t_3)$ (eq. (176)) to second order in $\lambda$. However, as we have already mentioned in section 5.2, this limit depends on our choice of a zero-order Hamiltonian. For the sake of simplicity, we shall focus here on the special case where $H_a = H_c$ which implies that the states $|a\rangle$ and $|c\rangle$ have identical interactions with the bath. This is a common situation in molecular Raman spectra where $|a\rangle$ and $|c\rangle$ are usually different vibrational states of the ground electronic state whereas $|b\rangle$ belongs to an electronically excited state. This choice also eliminates some of the ambiguity in the choice of the zero-order Hamiltonian and simplifies the final result. We thus define

$$\lambda U = H_a - H_b = H_c - H_b; \quad (186)$$

with this choice it is more convenient to choose $H_a$ as our zero-order Hamiltonian. We therefore rewrite eq. (158) in the form:

$$F(t_1, t_2, t_3) = \left\langle \exp \left( i \lambda \int_0^\tau d\tau U(\tau) \right) \exp \left( -i \lambda \int_0^\tau d\tau U(\tau) \right) \exp \left( i \lambda \int_0^\tau d\tau U(\tau) \right) \right\rangle, \quad (187)$$

where

$$U(\tau) \equiv \exp(iH_a\tau) \, U \, \exp(-iH_a\tau). \quad (188)$$

Without loss of generality we may also set

$$\langle U \rangle = \text{Tr}_B(U\phi_2) = 0, \quad (189)$$

this can always be done by including $\langle U \rangle$ in $\omega_{ba}$ and using the transformation

$$\omega_{ba} \rightarrow \omega_{ba} + \langle U \rangle \quad (190a)$$

$$U \rightarrow U - \langle U \rangle. \quad (190b)$$

The weak coupling limit is now obtained by introducing the ansatz (eq. (176)) expanding eqs. (187) and (176) in $\lambda$ and comparing order by order. Eq. (189) implies

$$K_1 = 0 \quad (191)$$
so that the lowest order that contributes to eq. (176) is the second order. After a little bit of algebra, we finally get [48]

\[
F(t_1, t_2, t_3) = \exp\left\{-\lambda^2 \left[ g(t_1) + g(t_3) + g(t_2 - t_1) + g(t_3 - t_2) - g(t_2) - g(t_3 - t_1) \right] \right\} \tag{192}
\]

where

\[
g(\tau) = \int_0^\tau d\tau_1 (\tau - \tau_1) \langle U(\tau_1) U(0) \rangle = \int_0^\tau d\tau_1 \int_0^\tau d\tau_2 \langle U(\tau_1) U(\tau_2) \rangle. \tag{193}
\]

We note that in this case (unlike the more general expansion eqs. (182)), the information content of the two-photon experiment is identical to that contained in the single photon line shape eq. (104), i.e. the line broadening function \( g(\tau) \). Several ways for the evaluation of \( g(\tau) \) were already described in section 4 (quantum, semiclassical, hydrodynamic, etc.). A stochastic model was also developed recently by Takagahara Hanamura and Kubo [71]. Their final result was a special case of eq. (192) with \( g(\tau) \) given by eq. (136b).

(v) The factorization approximation

The factorization approximation (eq. (48)) developed in section 3 simplifies considerably the evaluation of the Raman spectrum. We note that, in general, the evaluation of \( F(t_1, t_2, t_3) \) is quite complicated. Moreover, even if we have \( F \), we still need to perform the triple integral eq. (154). The factorization approximation enables us to express the spectrum using the single photon line shapes \( I_{ab}^v \), \( I_{bc}' \), and \( I_{ac}' \). To that end let us introduce the projection operator:

\[
\hat{P} = \rho_a|aa\rangle \langle aa| + \rho_b|bb\rangle \langle bb| + \frac{1}{2}(\rho_a + \rho_c) [\langle ac| + |ca\rangle \langle ac|] \tag{194}
\]

where we define

\[
\rho_\nu = \exp(-H_\nu/kT)/\text{Tr} \exp(-H/kT), \quad \nu = a, b, c. \tag{195}
\]

Using eq. (194) and eq. (48), together with figure 8, we get:

\[
\langle cc|\hat{P}\tilde{P}\hat{P}|aa\rangle = \langle cc|\hat{P}\tilde{P}(\nu)\hat{P}|bb\rangle \langle bb|\hat{P}\tilde{P}(\nu)\hat{P}|bb\rangle + \langle cc|\hat{P}\tilde{P}(\nu)\hat{P}|ac\rangle \langle ac|\hat{P}\tilde{P}(\nu)\hat{P}|ac\rangle + \langle cc|\hat{P}\tilde{P}(\nu)\hat{P}|ca\rangle \langle ca|\hat{P}\tilde{P}(\nu)\hat{P}|ca\rangle. \tag{196}
\]

Eq. (196) together with (150) immediately results in:

\[
\hat{I}(\Delta_L, \Delta_a) = 2\mu_a^2 \mu_b^2 \frac{1}{\gamma_b} I_{ab}(\Delta_L) I_{bc}(\Delta_a) I_{ac}(\Delta_a) I_{ac}(\Delta_a) I_{ac}(\Delta_L) + \text{Im}[I_{ab}(\Delta_L - \Delta_a) I_{bc}(\Delta_a) I_{ac}(\Delta_a)]. \tag{197}
\]

(vi) The impact (Markovian) limit

The impact limit for the single photon line shapes was discussed in detail in section 4.3. Basically it
results in

\[ I_{\nu}(\Delta) = \frac{1}{-\Delta + i \Gamma_{\nu}}, \quad \nu = ab, cb, ac \]  \hspace{1cm} (198)

where \( \Gamma_{\nu} \) are given by eq. (130). Eq. (197) together with (198) is the common result that is obtained using the Bloch equations [29].

Upon the substitution of eqs. (198) in eq. (197) we finally get:

\[ \hat{I}(\Delta_L, \Delta_a) = \frac{2 \mu_1^2 \mu_2^2}{\Delta_L^2 + \Gamma_{ab}^2} \left\{ \pi \delta(\Delta_a - \Delta_L) + \frac{2 \Gamma_{ab}}{\gamma_b} \frac{\Gamma_{bc}}{\Delta_a^2 + \Gamma_{bc}^2} \right\} \]  \hspace{1cm} (199)

where for the sake of simplicity we have also taken

\[ \gamma_a = \gamma_c = 0 . \]  \hspace{1cm} (200)

We recall that in this case

\[ \Gamma_{ab} = \frac{1}{2} \gamma_b + \hat{\Gamma}_{ab} \]  \hspace{1cm} (201a)

\[ \Gamma_{bc} = \frac{1}{2} \gamma_b + \hat{\Gamma}_{ac} . \]  \hspace{1cm} (201b)

We have performed some numerical calculations of eq. (197) where \( I_{\nu a}(\Delta) \) are given by eq. (104) with \( g(\tau) \) denoted as \( g_{\nu a}(\tau) [76, 77] \). We have further assumed that levels \( |a\) and \( |c\) have identical interactions with the bath. This applies for instance to molecular spectra when \( |a\) and \( |c\) are different vibrational levels of the ground electronic state and \( |b\) belongs to an excited electronic state. As a result \( U_a = U_c \) in eq. (3) and we get:

\[ g(\tau) \equiv g_{ab}(\tau) = g_{cb}(\tau) \]  \hspace{1cm} (202a)

and

\[ g_{ac}(\tau) = 0 . \]  \hspace{1cm} (202b)

\( g(\tau) \) was taken from the stochastic line shape theory of Kubo (eq. (136)), and we have calculated \( \hat{I}(\Delta_L, \Delta_a) \) using \( \kappa = 10 \) (impact) and \( \kappa = 0.1 \) (static) line profiles for \( I_{ab}(\Delta) \).

In fig. 9 we show the line profiles for both cases. At \( \Delta_L = 0 \) we see two components. A narrow (Raman) component at \( \Delta_a = \Delta_L \) and a broad (redistribution) component at \( \Delta_a = 0 \). The \( \delta \) and \( \Lambda \) parameters for the \( \kappa = 10 \) and \( \kappa = 0.1 \) lines are chosen so that \( I''_{ab}(\Delta) \) has the same full width at half maximum. As \( \Delta_L \) is detuned, the ratio of integrated intensities of the redistribution and Raman components does not change in the impact limit \( \kappa = 10 \) (right column) and is equal to \( 2 \hat{\Gamma}_{ab}/\gamma_b \). This may easily be seen using eq. (199). In the other extreme \( \kappa = 0.1 \) (left column) we see how the redistribution term gradually disappears. This may be interpreted by saying that \( \hat{\Gamma}_{ab} \) is actually frequency dependent \( \hat{\Gamma}_{ab}(\Delta_L) \), and it vanishes at large detunings, where the impact limit fails [24]. In the present formulation we do not need to invoke this argument and the vanishing of the redistribution component arises naturally from the frequency dependence of the actual line shape function \( I''_{ab}(\Delta) \).
6. Absorption line shapes in a strong radiation field

In this section we make the first application of the tetradic scattering formulation towards the calculation of a multiphoton process. We shall consider the simplest example, namely a two-level system interacting with a single mode of a strong radiation field [78–81]. Unlike the weak field spectra
considered in sections 4 and 5, the $T_1$ relaxation mechanism is playing now an active role in the process. In fact, the inclusion of a $T_1$ relaxation is necessary in order to define a line shape in a strong field. In the absence of a $T_1$ relaxation mechanism the populations of the two levels will be equalized at steady state and there will be no absorption of radiation. The adequate description of the $T_1$ relaxation will now be done as follows. We start with the system states which are identical to those of section 4, i.e.

\begin{align}
|a\rangle &= |\bar{a}, n_L\rangle \\
|b\rangle &= |\bar{b}, n_L - 1\rangle.
\end{align}

The Liouville equation for the entire system (absorber, plus bath plus field) is:

$$\frac{d\rho}{dt} = -iL\rho$$

where $L$ is the Liouville operator.

$$L = [H, ] + \tilde{L}.$$  

Here $H$ is given by eq. (1) (without the $\gamma_a$ and $\gamma_b$ terms which will be included in $\tilde{L}$). $\tilde{L}$ is the $T_1$ relaxation matrix given by

\begin{align}
\tilde{L}_{aa,aa} &= -\tilde{L}_{bb,aa} = -i\gamma_a, \\
\tilde{L}_{bb,bb} &= -\tilde{L}_{aa,bb} = -i\gamma_b, \\
\tilde{L}_{ab,ab} &= \tilde{L}_{ba,ba} = -\frac{1}{2}i\gamma,
\end{align}

where

$$\gamma = \gamma_a + \gamma_b.$$  

$\tilde{L}$ is assumed to arise from a coupling to some other bath with a short correlation time (e.g. spontaneous emission, inelastic collisions) and is responsible for the relaxation of our two-level system (in the absence of driving, $\mu_L = 0$) to thermal equilibrium, i.e.

$$\tilde{P}_b = \gamma_a/\gamma,$$

$$\tilde{P}_a = \gamma_b/\gamma.$$  

Using eq. (27) and fig. 2, the strong field absorption line shape is given by

$$\hat{I}_{ab}(\Delta) = i\langle aa|\mathcal{T}(0)|\rho(-\infty)\rangle.$$  

The initial density matrix $\rho(-\infty)$ is

$$\rho(-\infty) = \tilde{P}_a\rho_a|a\rangle\langle a| + \tilde{P}_b\rho_b|b\rangle\langle b|.$$  

\( \rho_a \) and \( \rho_b \) were introduced in eq. (195). In Liouville tetradic notation, eq. (209) reads

\[
|\rho(-\infty)) = \bar{P}_a|\rho_a(\text{aa})\rangle + \bar{P}_b|\rho_b(\text{bb})\rangle.
\]

(210)

Upon substituting eq. (210) in (208) and recalling that

\[
\mathcal{V}|\text{aa}\rangle = \mu_L(|\text{ba}\rangle - |\text{ab}\rangle) = -\mathcal{V}|\text{bb}\rangle,
\]

(211)

we get

\[
\hat{I}_{ab}(\Delta) = i(\bar{P}_a - \bar{P}_b) \langle \text{aa}|\mathcal{F}(0)|\rho_a(\text{aa})\rangle.
\]

(212)

At this stage we introduce the tetradic projection operator:

\[
\hat{P} = |\rho_a(\text{aa})\rangle \langle \text{aa}| + |\rho_b(\text{bb})\rangle \langle \text{bb}|
\]

(213)

and the complementary projection

\[
\hat{Q} = 1 - \hat{P},
\]

(214)

in terms of which we may write

\[
\hat{I}_{ab}(\Delta) = i(\bar{P}_a - \bar{P}_b) \langle \text{aa}|\mathcal{F}(0)\hat{P}|\text{aa}\rangle.
\]

(215)

\( \hat{P}\mathcal{F}\hat{P} \) will now be evaluated using eqs. (44). \( \hat{P} \) converts \( \mathcal{F} \), \( R \) and \( G \) to 2x2 matrices in the \( |\text{aa}\rangle, |\text{bb}\rangle \) space. Using eqs. (44b) and (211), it is clear that

\[
\langle \text{aa}|\hat{P}\mathcal{F}\hat{P}|\text{aa}\rangle = \langle \text{bb}|\hat{P}\mathcal{F}\hat{P}|\text{bb}\rangle = -\langle \text{bb}|\hat{P}\mathcal{F}\hat{P}|\text{aa}\rangle = -\langle \text{aa}|\hat{P}\mathcal{F}\hat{P}|\text{bb}\rangle
\]

(216)

we thus have:

\[
\hat{P} R(\omega) \hat{P} = \langle \text{aa}|\hat{P} R(\omega) \hat{P}|\text{aa}\rangle \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}
\]

(217)

similarly \( \hat{P} G_s(\omega) \hat{P} \) is given by

\[
\hat{P} G_s(\omega) \hat{P} = \begin{pmatrix} \omega + i\gamma_b & -i\gamma_b \\ -i\gamma_b & \omega + i\gamma_a \end{pmatrix}^{-1} = \frac{1}{\omega(\omega + i\gamma)} \begin{pmatrix} \omega + i\gamma_b & i\gamma_b \\ i\gamma_a & \omega + i\gamma_a \end{pmatrix}.
\]

(218)

Multiplying eqs. (217) and (218) and letting \( \omega \to 0 \) we get:

\[
\hat{P} G(0) \hat{P} R(0) \hat{P} = \langle \text{aa}|\hat{P} R(0) \hat{P}|\text{aa}\rangle \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}.
\]

(219)

Upon substitution of eqs. (44), (217) and (219) in eq. (215) we finally get [81]:
\[ \hat{I}_{ab}(\Delta) = (\vec{P}_a - \vec{P}_b) \frac{\chi(\Delta)}{1 + (2/\gamma) \chi(\Delta)} \] 
\hspace{1cm} (220)

where

\[ \chi(\Delta) = i\langle aa|\hat{P} R(0) \hat{P}|aa\rangle. \] 
\hspace{1cm} (221)

\[ \chi(\Delta) \] may be expanded in powers of \( \mu_L \) resulting in:

\[ \chi(\Delta) = \mu_L^2 \chi^{(2)} - \mu_L^4 \chi^{(4)} + \mu_L^6 \chi^{(6)} + \cdots \] 
\hspace{1cm} (222)

so that

\[ \hat{I}_{ab}(\Delta) = (\vec{P}_a - \vec{P}_b) \frac{\mu_L^2 \chi^{(2)}(\Delta) - \mu_L^4 \chi^{(4)}(\Delta) + \cdots}{1 + (2/\gamma) [\mu_L^2 \chi^{(2)}(\Delta) - \mu_L^4 \chi^{(4)}(\Delta) + \cdots]} \] 
\hspace{1cm} (223)

To lowest order in \( \mu_L \) (eq. (46))

\[ \hat{P} R^{(2)} \hat{P} = \hat{P} \mathcal{F}^{(2)} \hat{P}. \] 
\hspace{1cm} (224)

Eqs. (221) together with (224) yield

\[ \chi^{(2)}(\Delta) = 2I''_{ab}(\Delta) \] 
\hspace{1cm} (225)

if we truncate the expansion (222) and retain only \( \chi^{(2)} \) we get an expression for the line shape in a strong field, expressed in terms of the ordinary, weak-field, line shape, \( I''_{ab} \) i.e.

\[ \hat{I}_{ab}(\Delta) = (\vec{P}_a - \vec{P}_b) \frac{2\mu_L^2 I''_{ab}(\Delta)}{1 + (4/\gamma) \mu_L^2 I''_{ab}(\Delta)} \] 
\hspace{1cm} (226)

where we recall the normalization:

\[ \int I''_{ab}(\Delta) \, d\Delta = \pi. \] 
\hspace{1cm} (227)

Eq. (226) with (227) is an important result of this section and enables us to express the strong field line shape \( \hat{I}_{ab}(\Delta) \) in terms of the ordinary weak-field profile \( I''_{ab}(\Delta) \). In general, however, the line shape depends also on \( \chi^{(4)}, \chi^{(6)} \) etc. which contain higher order dipole correlation functions [81]. Thus, the non-linear line shape contains more detailed information regarding the collision than the ordinary weak field line.

We shall now discuss eq. (226) and consider some limiting cases. We first note that in weak radiation fields (to lowest order in \( \mu_L \)) eq. (226) reduces to:

\[ \hat{I}(\Delta) = 2(\vec{P}_a - \vec{P}_b) \mu_L^2 I''_{ab}(\Delta). \] 
\hspace{1cm} (228)
In the impact limit we have (eq. (131) with $\Delta' = 0$):

$$I_{ab}(\Delta) = \frac{I_{ab}}{\Delta^2 + I_{ab}^2} \tag{229}$$

Upon substitution of eq. (229) in eq. (226) we finally get

$$\tilde{I}_{ab}(\Delta) = (\tilde{P}_a - \tilde{P}_b) \frac{2\mu_L^2 \Gamma_{ab}}{4\mu_L^2 \Gamma_{ab}/\gamma + \Delta^2} \tag{230}$$

This is the well known formula describing a Lorentzian line in a weak field ($\mu_L \to 0$) which is power broadened at strong fields when $\mu_L$ is comparable to $\sqrt{\tau_{ab} \gamma}$. Eq. (230) may be obtained directly from the Bloch equations and was first derived in the context of pressure broadening by Karplus and Schwinger [79].

We have calculated the line shape function eq. (226), where $I_{ab}(\Delta)$ was evaluated using eqs. (104) and (136) [81]. The results are given in figs. 10 and 11 for various values of the Rabi frequency $\mu_L$. Figure 10 shows the impact line shape ($\kappa = 10$) and fig. 11 shows a non-impact case ($\kappa = 1$).

As is clearly seen from fig. 10 $\tilde{I}_{ab}(\Delta)$ remains a Lorentzian in this case even for strong saturating fields $\mu_L$. In fig. 11, on the other hand, the line shape changes its form significantly as $\mu_L$ increases. It may be shown that in the impact limit $\chi^{(2)} = \chi^{(6)} = \cdots = 0$ and eq. (226) becomes exact [81].

Fig. 10. The saturation behavior of the absorption line shape [81] (eq. (226) together with (104) and (136)) in the Markovian limit $\kappa = 10$. The frequency scale is set by taking $\gamma = 1$. In these units we have $\delta = 100, A = 1000$. 
7. Resonance Raman spectra in a strong radiation field

We shall now consider a more complicated example of a multiphoton process: A three level system interacting with a strong radiation field \[76, 77, 82-88\]. The model system is essentially identical to that of section 5 and will again apply to Raman spectra and to two-photon absorption as well (see fig. 7 and fig. 8). However there are two differences: We are looking for a solution of \(\langle \langle c|\mathcal{F}(0)|aa\rangle \rangle\) which is non-perturbative (infinite order) in \(\mu_\lambda\) but still to second order in \(\kappa\). Secondly, we shall introduce a more elaborate \(T_1\) relaxation matrix in which the three-level system is closed under relaxation and relaxes to level \(|a\rangle\) in the absence of driving \((\mu_\lambda = 0)\). As was already mentioned in the previous section, the \(T_1\) mechanism is playing an important role in a strong field and our result depends on the details of the \(T_1\) relaxation mechanism. The time evolution of the entire (absorber plus bath plus laser and scattered field modes) density matrix \(\rho\) is given by the Liouville equation:

\[
\frac{d\rho}{dt} = -iL\rho,
\]

where

\[
L = [H, \ ] + \tilde{L} = L_0 + \tilde{L}
\]

is the Liouville operator. Here \(H\) is the Hamiltonian (eq. (1), with \(\gamma_\alpha = \gamma_\beta = \gamma_\epsilon = 0\)) and \(\tilde{L}\) is the \(T_1\) relaxation matrix. We assume that the three-level system is closed under relaxation which proceeds only downwards on the energy scale, i.e. \(\tilde{L}\) is a \(3 \times 3\) matrix in the space of level populations,
\[
\mathbf{\tilde{L}} = -i \begin{pmatrix}
\gamma_b & 0 & 0 \\
-\gamma_{cb} & \gamma_c & 0 \\
-\gamma_{ab} & -\gamma_c & 0
\end{pmatrix}
\] (233)

where the rows and columns are labelled in decreasing order on the energy scale (bb, cc and aa).

The level relaxation rates \( T_1 \) for the levels \(|b\rangle\) and \(|c\rangle\) are given by \( \gamma_b \) and \( \gamma_c \) respectively, and we assume \( \gamma_a = 0 \) (|a\rangle being the ground state of the system). The \( b \rightarrow c \) and \( b \rightarrow a \) cross relaxation rates \( \gamma_{cb} \) and \( \gamma_{ab} \), satisfy

\[
\gamma_{cb} + \gamma_{ab} = \gamma_b .
\] (234)

We assume that initially (at \( t \rightarrow -\infty \)) the bath and the system are uncorrelated and \( \rho(-\infty) \) is given by eq. (52). Using eq. (37) and fig. 8, the Raman spectrum for arbitrary field strength is given by

\[
I(\Delta_\alpha, \Delta_\beta) = -i \langle cc | \tilde{\mathcal{F}}(0) | \rho(-\infty) \rangle .
\] (235)

We now introduce the following tetradic projection operator:

\[
\hat{P} = \rho_a\langle aa \rangle \langle aa | + \rho_b\langle bb \rangle \langle bb | + \rho_c\langle cc \rangle \langle cc | + \frac{1}{2}(\rho_a + \rho_c) \langle [ca] | + \langle [ac] | \langle [ac] 
\]

and its complementary projection operator

\[
\hat{Q} = 1 + \hat{P} .
\] (236b)

The spectrum in eq. (235) is given by matrix elements of \( \hat{P} \tilde{\mathcal{F}}(0) \hat{P} \), i.e.

\[
I(\Delta_\alpha, \Delta_\beta) = -i \langle cc | \hat{P} \tilde{\mathcal{F}}(0) \hat{P} | aa \rangle .
\] (237)

The \( \hat{P} \) projection operator (eq. (236a)) converts \( \tilde{\mathcal{F}} \) into a \( 5 \times 5 \) matrix in the space \( \{|aa\rangle, |bb\rangle, |cc\rangle, |ac\rangle \) and \( |ca\rangle \). This matrix will be evaluated using eqs. (44). We have thus to find the \( 5 \times 5 \) \( \hat{P} \hat{R} \hat{P} \) matrix.

We recall that since we are using a weak probe (\( \mu_s \) is small) we need to evaluate \( \hat{P} \hat{R} \hat{P} \) (and \( \hat{R} \hat{P} \hat{R} \)) to second order in \( \mu_s \) and to infinite order in \( \mu_L \). Therefore some of the matrix elements of \( R \) are to zero order in \( \mu_s \), others are first order in \( \mu_s \) and the rest are second order in \( \mu_s \). We shall denote these by \( R^{(0)} \), \( R^{(1)} \) and \( R^{(2)} \) respectively.

After some straightforward algebraic manipulations we may rewrite eq. (237) in the form \([76, 77]\):

\[
I(\Delta_\alpha, \Delta_\beta) = \frac{1}{1 - (2/\gamma_b) \chi_1(\Delta_L)} \left\{ \chi_2(\Delta_L, \Delta_s) - \frac{1}{\gamma_b} \chi_1(\Delta_L) \left[ \chi_2(\Delta_L, \Delta_s) + \chi_3(\Delta_L, \Delta_s) \right] \right. \\
+ \text{Im} \left[ \frac{\chi_2(\Delta_L, \Delta_s)}{[I_{ac}(\Delta_L - \Delta_s)]^{-1} - \chi_2(\Delta_L, \Delta_s)} \left[ \chi_2(\Delta_L, \Delta_s) - \frac{1}{\gamma_b} \chi_1(\Delta_L) \left[ \chi_2(\Delta_L, \Delta_s) + \chi_3(\Delta_L, \Delta_s) \right] \right] \right\}
\] (238)

where

\[
\gamma'_b = \gamma_b \left( 1 + \frac{\gamma_{cb}}{2 \gamma_c} \right)^{-1}.
\] (238a)
Here

\[\chi_1(\Delta_1) = -i\langle aa|\hat{P}R^{(0)}(0)\hat{P}|aa\rangle\]  
\[\chi_2(\Delta_1, \Delta_2) = \langle ac|\hat{P}R^{(0)}(0)\hat{P}|ac\rangle\]  
\[\chi_3(\Delta_1, \Delta_3) = \langle cc|\hat{P}R^{(1)}(0)\hat{P}|ac\rangle\]  
\[\chi_4(\Delta_1, \Delta_4) = \langle ac|\hat{P}R^{(1)}(0)\hat{P}|aa\rangle\]  
\[\chi_5(\Delta_1, \Delta_5) = \langle ac|\hat{P}R^{(1)}(0)\hat{P}|bb\rangle\]  
\[\chi_6(\Delta_1, \Delta_6) = -i\langle cc|\hat{P}R^{(2)}(0)\hat{P}|aa\rangle\]  
\[\chi_7(\Delta_1, \Delta_7) = -i\langle cc|\hat{P}R^{(2)}(0)\hat{P}|bb\rangle\]  

The functions \(\chi_i\) \((i = 1, \ldots, 7)\) contain the interaction with the external field to an arbitrary order (all orders in \(\mu_1\)). The functions \(\chi_1\) and \(\chi_2\) are to zeroth order in \(\mu_0\), \(\chi_3\), \(\chi_4\) and \(\chi_5\) are to first order in \(\mu_0\), and \(\chi_6\) and \(\chi_7\) are to second order in \(\mu_0\). They can be expanded in powers of \(\mu_L\) as follows:

\[\chi_i = \mu_L^2\chi_i^{(2)} + \mu_0^4\chi_i^{(4)} + \cdots \quad (i = 1, 2),\]  
\[\chi_j = \mu_0\mu_L\chi_j^{(2)} + \mu_0^3\chi_j^{(4)} + \cdots \quad (j = 3, 4, 5),\]  

and

\[\chi_k = \mu_L^2\chi_k^{(2)} + \mu_0^2\mu_L^2\chi_k^{(4)} + \cdots \quad (k = 6, 7).\]

In general, the \(\chi_i^{(n)}\) \((i = 1, 2, \ldots, 7; n = 2, 4, \ldots)\) terms involve \(n\)-time correlation functions and therefore knowledge of successively higher-order correlation functions is needed for the calculation of the line shape when the field strength is increased (already in the weak-field limit, four time correlation functions had to be introduced). Thus, in principle, the information content of the PRS experiments increases with the applied field strength. However, although formal expressions for the \(\chi_i\)'s were recently given \([76, 77]\), their evaluation in terms of \(n\)-time correlation functions \((n > 2)\) is quite tedious and will not be discussed here.

In the following we consider only the contribution of the two-time correlation functions \(\chi_i^{(2)}\) to the Raman line shape. Terms involving \(\chi_i^{(4)}\) and higher orders in the expansion (240) contain integrals over \(n\)-time correlation functions (with \(n \geq 4\)) resulting in increasing powers of \(\mu_L/A\) where \(A^{-1}\) is the correlation time usually associated with the duration of a single collision. Hence, if the external field is not too strong, i.e. if the condition \(\mu_L \ll A\) is satisfied, we can consider only the \(\chi_i^{(2)}\) \((i = 1, \ldots, 7)\) terms in the expansion (240).

In this case, the operator \(\hat{P}R\hat{P}\) (eq. (44b)) can be written as

\[\hat{P}R(\omega)\hat{P} = \hat{P}V\hat{P} + \hat{P}V\hat{Q} \frac{1}{\omega - \hat{O}L_0\hat{Q} - \hat{Q}\hat{L}\hat{Q}}\hat{O}V\hat{P},\]  

(241)
and within the space spanned by the states $|bc\rangle$, $|cb\rangle$, $|ab\rangle$ and $|ba\rangle$, $\hat{Q}$ can be replaced by the unit operator; we can write

$$\hat{P} R(\omega) \hat{P} = \hat{P} R(\omega) \hat{V} \gamma \hat{P},$$

using eqs. (239) and (240) we obtain

$$\chi^{(2)}_i = -2I^*_{ab}(\Delta_L)$$

$$\chi^{(2)}_2 = I_{bc}(-\Delta_s)$$

$$\chi^{(2)}_3 = I_{cb}(-\Delta_s)$$

$$\chi^{(2)}_4 = I_{ab}(\Delta_L)$$

$$\chi^{(2)}_5 = -[I_{ab}(\Delta_L) + I_{bc}(-\Delta_s)]$$

$$\chi^{(2)}_6 = 0,$$

and

$$\chi^{(2)}_7 = 2I^*_{bc}(-\Delta_s).$$

Upon substitution of eqs. (243) in eq. (238) we finally get [76, 77]:

$$\hat{I}(\Delta_L, \Delta_s) = \frac{2\mu_s^2 \mu_L^2}{1 + (4\mu_L^2 \gamma_b) I_{ab}(\Delta_L) \gamma_b} \left\{ \frac{2}{\gamma_b} I^*_{ab}(\Delta_L) I^*_{cb}(\Delta_s) \right. + \text{Im} \left[ \frac{1}{[I^*_{ac}(\Delta_L - \Delta_s)]^{-1} + \mu_L^2 \gamma_b \left[ I^*_{ac}(\Delta_L) + \frac{2\mu_s^2}{\gamma_b} I^*_{ab}(\Delta_L) I_{cb}(\Delta_s) \right]} \right\}$$

(244)

where we recall that the single photon line shape function $I_{ab}(\Delta)$ is given by eq. (104) and $I_{cb}$ and $I_{ac}$ are the corresponding line shapes for the cb and ac transitions respectively.

In the impact limit (eq. (131)) we have:

$$I_{\nu\mu}(\Delta) = \frac{1}{\Delta + i\Gamma_{\nu\mu}}, \quad \nu\mu = ab, cb, ac.$$  

(245)

Upon substituting eqs. (245) in eq. (244) we finally get [88b]:

$$\hat{I}(\Delta_L, \Delta_s) = \frac{2\mu_s^2 \mu_L^2 \gamma_b}{\Delta_L^2 + \Gamma_{ab}^2 + 4\mu_L^2 \Gamma_{ab} \gamma_b} \text{Im} \left\{ \left( \frac{(\Delta_s - \Delta_L + i\Gamma_{ac})}{(\Delta_s + i\Gamma_{cb})} \left( \frac{1}{\Delta_s + i\Gamma_{cb}} \right) \right) \right\}.$$  

(246)

In conclusion, we have derived a formal expression (eq. (238)) for the collision broadened Raman line shape, that is valid for arbitrary field strengths ($\mu_L$) and detunings ($\Delta_L, \Delta_s$). The line shape was then expanded in terms of the $\chi_i^{(n)}$ ($i = 1, 2, \ldots, 7; n = 2, 6, \ldots$) functions (eqs. (239)). The $\chi_i^{(2)}$ functions can
be expressed in terms of Laplace transforms of two-time correlation functions of the transition-dipole operators (in the interaction picture with respect to $H_a + H_b + H_c$). Similarly, the $\chi_i^{(n)}$ ($n > 2$) functions are related to $n$-time correlation functions [80, 81]. We should point out that since higher-order correlation functions appear with higher powers of the field strength ($\mu_L$) and the time integrations contribute powers of the correlation time $\tau^{-1}$ (usually associated with the duration of a single collision), the expansion (240) is actually an expansion in the dimensionless parameter $\mu_L/\Lambda$. We have considered the medium field strength case, defined by the condition

$$\mu_L / \Lambda \ll 1$$

(247)
i.e., although the field can be strong enough to saturate the ab transition (if $\mu_L \geq \frac{1}{2} \sqrt{\gamma_b I_{ab}}$), the period ($\mu_L^{-1}$) of the associated (on-resonance) Rabi oscillation is much longer than the collision time ($\tau^{-1}$) and hence, only single-photon absorption can occur during the collision with the perturber. In this approximation only the lowest order terms ($\chi_i^{(2)}$) in the expansion of the $\chi_i$’s contribute to the Raman spectrum which is thus completely determined by the two time correlation functions ($g_{ab}, g_{cb}, g_{ac}$). A similar result (valid only in the medium field limit) was recently obtained for the resonance fluorescence spectrum in a two-level system [89]. The advantage of the present approach is that the evaluation of the corrections (due to higher-order correlation functions) to the line shape is straightforward though somewhat tedious (using eqs. (238), (239) and (240) and expanding them in the radiative interaction $\gamma_L$)

A further advantage of the present method is that since the interactions with the laser and the scattered modes are treated on the same footing, it does not necessarily invoke the fluctuation regression approximation [90] which is perfectly valid only in the Markovian limit. Figures 12 and 13 show the variation of the RRS spectra (eq. (244)) with the pump intensity for resonance pumping ($\Delta_L = 0$) and for off-resonance pumping ($\Delta_L = 25$) [76, 77]. As in fig. 9, we have used the stochastic line shape function (eqs. (104) with (136)) for the single photon line shape $I_{ab}^\prime(\Delta)$. The right ($\kappa = 10$) column is in the impact limit and the left ($\kappa = 0.1$) column is in the static limit. The strong field is obtained whenever the generalized Rabi frequency

$$\theta = (\Delta_L^2 + 4\mu_L^2)^{1/2},$$

(248)
is the largest parameter in the problem (except for the inverse duration of a collision). The spectrum separates in this case into two (non-Lorentzian) peaks centered at

$$\Delta_s^{(\pm)} = \frac{1}{2}(\Delta_L \pm \theta).$$

(249)

In the weak field limit, the $\Delta_s^{(+)}$ peak reduces to the coherent Raman component (around $\Delta_s = \Delta_L$) and the $\Delta_s^{(-)}$ gives the incoherent redistribution component (around $\Delta_s = 0$). This gradual change is shown in figs. 12 and 13 as we move from bottom (strong field) to the top and is common to the impact and non-impact lines (right and left panels). The difference between the impact and non-impact lines is in the shape of the two peaks. We further note that the two equal components when $\mu_L$ is large, are much narrower in the static ($\kappa = 0.1$) case. This may again be interpreted by invoking the frequency dependence of $I_{ab}^\prime(\Delta)$ which exists at large detunings in $\kappa = 0.1$ case but is absent, by assumption, in the impact ($\kappa = 10$) case [24]. Figure 14 shows the variation of the Raman spectra with the detuning of the pump field for a finite intensity $\mu_L = 20$. We note that as $\Delta_L$ increases we need a stronger $\mu_L$ in order to achieve the asymptotic behavior mentioned above. Thus a $\mu_L = 20$ field is “strong” for $\Delta_L = 0$ (upper
Fig. 12. The saturation behavior of the resonance Raman spectrum $I(\Delta_L, \Delta_S)$ (divided by $\Delta \mu^2 \mu_0^2$) (eq. (244) together with (104) and (136)), for $\Delta_L = 0$, $\gamma_{eb} = 0$. Other parameters are the same as in fig. 9 [76, 77].

Fig. 13. The same as fig. 12 but for $\Delta_L = 25$ [76, 77].
Fig. 14. Variation of the resonance Raman spectrum \( \tilde{I}(\Delta_L, \Delta_s) \) (divided by 2\( \mu \tilde{I}(\mu) \)) (eq. (244)) with detuning \( \Delta_L \) for a finite Rabi frequency \( \mu_L = 20 \). Other parameters are the same as in fig. 12 [76, 77].

panels in fig. 14) and the spectra are split into two equal components. The same field for \( \Delta_L = 40 \) (lower panel) is weak and the two components are not equal, neither in their intensity nor in their width. We also see that the lines are narrower in the non-impact (\( \kappa = 0.1 \)) case. Finally we note that the two components are roughly equal in magnitude in the impact but a dramatic change occurs for the non-impact lines where the redistribution component disappears with the detuning.
8. Concluding remarks

In this review we had developed and applied the tetradic $T$ matrix together with the dressed atom picture, towards the microscopic calculation of single photon, two-photon and multiphoton processes. The model system, consisting of an absorber, the radiation field and a bath of foreign perturbers was introduced in section 2. In general an $n$ photon process is a probe for a $2n$-time correlation function of the material system which contains an enormous amount of information. In section 3 we developed the basic tetradic $T$ matrix formulation which enables us to define in a very convenient and straightforward way the complete information content of a given experiment in terms of the appropriate correlation functions (eq. (37)). The rest of this article is devoted to developing an approximation scheme and a hierarchy of useful approximations for the evaluation of these correlation functions.

Figure 1 is the basic bookkeeping device in the present formulation and provides a simple pictorial representation of the various correlation functions. We then developed the factorization approximation (eq. (48)) which enables us to express all multiphoton cross sections in terms of single photon complex line shape functions. If in addition to the above factorization we further assume that each single photon line shape is a simple Lorentzian (eq. (49a)), we recover the usual results of the Bloch equations.

Section 4 contains an overview of the treatment of collisional broadening of single photon processes (ordinary absorption). This is done since within the factorization approximation we use the single photon line shapes to construct the cross sections for multiphoton processes. Moreover, the same techniques are later used in section 5 to construct the cross sections for multiphoton processes (without invoking the factorization approximation). The expansions discussed in section 4 are the dressed cluster expansion (DCE) and the perturbative expansion. The dressed cluster expansion uses the few-body dynamics of small clusters (single perturber, two perturbers, etc.) but incorporates the exact static density correlation functions of the fluid. To lowest order the DCE reduces to the binary collision approximation. The perturbative expansion (in the interactions responsible for the line broadening) allows us to use exact dynamical correlation functions of the fluid which may be obtained by a variety of techniques (kinetic, semiclassical, numerical simulations, hydrodynamics, etc.).

Section 4.3 contains a summary of our final expressions for the single photon line shapes. The basic expression for the line shape function is eq. (104) where all the relevant information regarding the line shape is contained in the line broadening function $\tilde{g}(\tau)$. We then evaluated $\tilde{g}(\tau)$ using the cluster expansion (which to lowest order reduces to the binary collision approximation), semiclassical techniques, and the weak coupling approximation. We also considered the static and the impact (Markov) limits of slow and fast collisions respectively. The latter is the case where the Bloch equations apply. Finally, we presented the stochastic line shape function of Kubo (eq. (104) together with eq. (136)) which is a two-parameter function which interpolates between the static and the impact limits, and summarized the expressions for the spectral moments of the line shape.

In section 5, we considered two-photon processes (two-photon absorption and Raman spectra) (fig. 7). Figure 8 shows the three pathways (plus their c.c.) in Liouville space which contribute to two-photon processes. In general, we need apply two perturbations from the left and two from the right in order to get from $|aa\rangle$ to $|cc\rangle$. The various pathways differ in the order in time in which these perturbations are applied. The most general expression for the two-photon cross section is eq. (154) which is expressed in terms of the four time correlation function $F(t_1, t_2, t_3)$. Next, we generalized the expansion schemes developed in section 4 and applied them towards the evaluation of $F(t_1, t_2, t_3)$. Our final results for the line shape in the two-photon processes are the cluster expansion (eq. (178) together with (182)), the semiclassical cluster expansion (eq. (184)), the static limit (eq. (185)) and the weak coupling limit (eq.
The basic problem with these expressions is that they require a large computation effort (we need to evaluate a four point correlation function and then perform the triple Fourier transformation, eq. (154)). Such a calculation was performed so far only for the stochastic line shape function of Kubo [71] within the weak coupling limit (eq. (192)). Simpler expressions are therefore needed which will be easier to manipulate. We thus apply the factorization approximation (eq. (48)), which is the leading term in a systematic expansion (eq. (44)) and allows us to express all the relevant information in terms of products of two time correlations functions (i.e. ordinary, single photon, line shapes (eq. (197))). The latter may then be evaluated by one of the many methods discussed in section 4. As shown in eq. (48) this approximation is not limited to two-photon processes and may be used for any multiphoton process as well. The usual result of the Bloch equations (eq. (199)) is shown to be the outcome of two successive approximations; (i) the factorization approximation, and (ii) a Markov approximation for each single photon line shape which is thereby expressed as a complex Lorentzian amplitude (eq. (198)). Eq. (197) relaxes approximation (ii) and provides a simple and useful non-impact result for two-photon spectra.

Section 6 is devoted to multiphoton absorption of a two-level system in a strong field. We developed a simple expression (eq. (226)) which reduces to the unified theory of spectral line shapes in a weak field and to the Karplus–Schwinger formula (eq. (230)) in the impact limit. Finally in section 7 we treated the problem of resonance Raman spectra in a strong radiation field. We derived a unified expression (eq. (244)) which reduces in a weak field to the two-photon cross section within the factorization approximation (eq. (197)) and in the impact limit to the usual results of the Bloch equations (eq. (246)). In both sections, 6 and 7, we used the techniques of sections 3 and 4 together with the factorization approximation (eq. (48)).

In conclusion we shall now summarize the main advantages of the present formalism.

1. The radiation field is treated quantum mechanically (the "dressed atom" picture) so that spontaneous emission is properly taken into account.

2. We present a unified description valid for all kinds of multiphoton processes. One of the basic problems in the field of quantum optics arises since the workers in the field come from very different disciplines. As a result there were many languages and terminologies developed to interpret the same types of experiments. Each new peak is given a name (usually a three word name with a three or four letter acronym . . . ) and one often gets the false impression that a new theoretical framework is needed for each slight modification of an experiment. This review is an attempt to demonstrate how a common microscopic language and formalism may be applied to all of these phenomena.

3. We are able to adjust the level of input information to the information content of the experiment. The complete information in an \( n \) photon experiment is the \( 2n \)-time correlation function and we show how to calculate it using the complete microscopic Hamiltonian (the potentials of interaction). We further show how this amount of information is considerably reduced in the factorization impact limit where the Bloch equations apply. One is able therefore to choose the desired level of theoretical description all the way from a complete microscopic theory of the bath to the Bloch equations where a few \( T_1 \) and \( T_2 \) constants are sufficient. It should be noted that it is a common procedure to generalize the Bloch equations to account for non-impact line shapes by putting frequency dependent relaxation constants \( T_1(\omega) \) and \( T_2(\omega) \) [24, 54]. This is, however, a phenomenological fitting procedure rather than a real theory. Moreover, this approach may lead to erroneous results in highly non impact situations [43].

4. Other types of baths (phonons, intramolecular interactions in large molecules, etc.) can easily be incorporated within the present formalism.

For the sake of clarity in the presentation we considered only steady state single absorber
phenomena and did not deal with polarization [55], cooperative effects [1] or time resolved experiments [23, 56]. The present formalism can be extended to incorporate all of these effects without a major difficulty.

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Note added in proof

(1) In eq. (29b) of ref. [77], there were a few misprints which were corrected in eq. (244) of the present article.

(2) In the present review, we focused, for the sake of clarity, on ideal steady state experiments where the radiation fields are coherent and monochromatic. Another type of problems of current interest arises from the fact that in real life the laser fields are not ideal (coherent, monochromatic) but exhibit some stochastic elements (e.g., phase fluctuations, amplitude fluctuations, etc.). A theoretical treatment of the effects of these fluctuations on multiphoton line shapes is therefore both of fundamental and practical importance. These processes introduce additional dephasing and damping time scales into the problem and may enable us to learn more about the microscopic dynamics. [See e.g. A.T. Georges and P. Lambropoulos, Phys. Rev. A20 (1979) 991; A. Zoller, Phys. Rev. A20 (1979) 1019; L. Mandel and H.J. Kimble, in ref. [4] p. 119; J. Cooper and A. Szoke, Phys. Rev. A23 (1981) 378.] The inclusion of these effects in the present approach is straightforward. In the two photon spectra e.g., all we have to do is to set

\[ F(\tau_1, \tau_2, \tau_3, \tau_4) \rightarrow \langle E_L(\tau_1) E_L(\tau_4) \rangle \langle E_s(\tau_2) E_s(\tau_3) \rangle \cdot F(\tau_1, \tau_2, \tau_3, \tau_4) \]

i.e., we should simply multiply \( F \) (eq. (154)) by the appropriate correlation functions of the external fields \( E_L \) and \( E_s \). (Note that \( V_L \) acts at times \( \tau_1 \) and \( \tau_4 \) and \( V_s \) acts at times \( \tau_2 \) and \( \tau_3 \).) In the case of Raman or fluorescence processes, \( E_s \) comes from coupling with vacant modes of the radiation field. In this case, we should multiply \( F \) by \( \langle E_L(\tau_1) E_L(\tau_4) \rangle \) only. If the field correlation functions \( \langle E(\tau) E(\tau') \rangle \) are exponential in \( \tau - \tau' \) this simply amounts to the addition of another dephasing process to the problem. A theory for these effects together with a microscopic treatment of time-resolved observables and four wave mixing spectra for our model Hamiltonian (eq. (1)) was developed recently using the formalism introduced in this article (S. Mukamel, to be published).

(3) I would like to mention here the recent review article by L. Allen and C.R. Stroud (Physics Reports 91 (1982) 1) which covers methods of calculating multiphoton absorption line shapes in the impact limit where the Bloch equations apply.