an obvious absurdity. Thus, the argument is completed. The only solution of Eq. (14) is not a solution of Eq. (12a) and thus Eqs. (12a) and (12b) have no common solution.

IV. DISCUSSION

WM characterize their results for the energy of helium through third order as "somewhat discouraging" and a number of physicists have taken the WM calculation to indicate that the Hartree-Fock approximation is a poor zeroth-order approximation for perturbation theory. We have shown, on the contrary, that *no* conclusion may be drawn about the Hartree-Fock approximation on the basis of the WM paper. WM used the Hartree, rather than the Hartree-Fock, approximation and our proof in Sec. III indicates that the first-order functions for the two models are different.

ACKNOWLEDGMENTS

One of the authors (JS) is extremely grateful to Dr. M. Cohen for pointing out the arresting behavior of the E_3 calculation in a preprint of the WM paper and for a number of conversations and a correspondence in the latter half of 1963. We wish, also, to thank Dr. A. W. Weiss for sending some of the output of the WM code.

PHYSICAL REVIEW VOLUME 141, NUMBER 1 JANUARY 1966

Symmetry Considerations in Pressure-Broadening Theory

A. Ben-Reuven*
National Bureau of Standards, Washington, D. C.

(Received 11 August 1965)

Symmetry properties of the Zwanzig-Fano relaxation matrix are studied. Its invariance under rotations and inversion is proven for isotropic gases, to all orders in the gas density. Each multipole radiation operator is confined to a distinct invariant subspace in the Liouville space of operators. These invariant subspaces form the basis for the reduction of the relaxation matrix; therefore, the various multipole spectra are broadened independently. Properties of the relaxation matrix under Liouville conjugation are studied, and expressions are given relating matrix elements in which Liouville-conjugate pairs of vectors are involved.

1. INTRODUCTION

PRESSURE-broadening theory has progressed considerably since the pioneering work of Anderson[1] who first introduced systematically quantum-mechanical methods to describe the effects of collisions of molecules on the spectra of dilute gases. Notable steps in the development of the theory were the extension to overlapping lines by Baranger[2] and by Kolb and Griem,[3] the full quantum-mechanical treatment, in the impact approximation, by Baranger,[2] and the introduction by Fano[4] of statistical-mechanical methods to present pressure broadening as a relaxation process, and to include non-Markoffian effects of the collisions.

A step initiated by Baranger, and fully appreciated and developed by Fano, was the introduction of a convenient language for the description of pressure broadening, i.e., the Liouville-space formalism. The Liouville operator describes the infinitesimal variation in time of the density matrix in statistical mechanics. Its eigenvalues are resonance frequencies rather than energy levels of a system; and its eigenvectors are the corresponding transition operators.[5] This formalism is appropriate because pressure broadening concerns each transition as a whole, and cannot be simply related to the relaxation of the individual energy eigenstates. In the limit of zero pressure the resonance frequencies are simply related to the energy levels by the combination principle[6]

$$\omega_{if}=E_i-E_f.$$

The effects of collisions on the energy eigenstates can be described by a transition matrix $t(E)$ which obeys the Lippmann-Schwinger equation. Fano similarly defines a transition matrix $\mathbf{m}(\omega)$ which obeys a Lippmann-Schwinger equation in Liouville space, and from which all pressure-broadening effects may be derived. However, the relation of $\mathbf{m}(\omega)$ to $t(E)$ is the monstrous Eq. (55) of Ref. 4.

The Liouville-space representation expresses the shape of the spectrum by a set of parameters, which form the so-called *relaxation matrix*[7] $\langle \mathbf{M}_c(\omega)\rangle$. In the

---

* Present address: Weizmann Institute of Science, Rehovoth, Israel.

[1] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[2] M. Baranger, Phys. Rev. **111**, 481; **111**, 494; **112**, 855 (1958).

[3] A. C. Kolb and H. Griem, Phys. Rev. **111**, 514 (1958).

[4] U. Fano, Phys. Rev. **131**, 259 (1963), to be referred to hereafter as F.

[5] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).

[6] The same units (i.e., rad/sec) will be used throughout this work for frequencies as well as energies.

[7] Defined in Ref. 4 by the methods of R. Zwanzig [*Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106].

impact approximation,[2] where the relaxation matrix is independent of the frequency, and proportional to the pressure, the line-shape expression, as a function of the frequency and the pressure, attains a particularly simple form, notwithstanding the great difficulties encountered in actual theoretical evaluation of the relaxation matrix elements. The advantage of this approach has been recently demonstrated in explaining the behavior of the ammonia inversion spectrum in the microwave region, which had not been understood hitherto.[8] It appears now that this peculiar behavior is of a quite broader occurrence in microwave spectra at elevated pressures.

The problem of microwave line shapes, in general, and of the ammonia inversion spectrum, in particular, form the subject matter of a separate publication.[9] The purpose of this article is to study further the formal properties of pressure broadening in its Liouville-space representation, in the spirit of complementing the work of Fano.

An opening section is devoted to discussion of some of the underlying hypotheses of the theory. Next follows a discussion of invariance under the rotation-inversion symmetry group, and the resulting reduction of the relaxation matrix. It is concluded that lines belonging to different multipole spectra are never coupled when pressure broadened by isotropic gases. In case the same transition is allowed by several multipole selection rules, it may be considered as a superposition of lines of distinct multipole species, each broadened and shifted differently.

In the final section the concept of Liouville conjugation is introduced. This operation interchanges the initial and final states of any transition and reverses the sign of all resonance frequencies. Relations are derived for relaxation-matrix elements involving conjugate pairs of Liouville-space vectors.

2. A HIERARCHY OF APPROXIMATIONS

The absorption coefficient $\alpha(\omega)$ of a gas is usually defined in the limit of weak radiation fields, where the gas is assumed to be in thermal equilibrium. If we knew the complete energy spectrum of the gas, we could write down the absorption coefficient, for radiation of a particular multipole species, as

$$\alpha(\omega)=\text{const}\times\mathcal{V}^{-1}\omega\sum\nolimits_{FI}\delta(\omega-\omega_{IF})(\rho_F-\rho_I)|X_{FI}|^2, \quad (1)$$

where I,F are the sets of quantum numbers labeling the upper and lower levels, respectively, giving rise to a transition with frequency $\omega_{IF}=\omega$; $\mathcal{V}$ is the volume of the gas sample, X is the total multipole operator of the gas, and ρ is its (equilibrium) density matrix. The difference $\rho_F-\rho_I$ expresses the subtraction of induced emission from absorption. Thanks to the Dirac δ function in (1), we may insert

$$\rho_F-\rho_I=(e^{\hbar\omega/kT}-1)\rho_I$$

and confine the calculation to, say, induced emission alone. In terms of the Liouville operator $\mathbf{L}$ [Eq. (F8)], Eq. (1) becomes

$$\alpha(\omega)=-\text{const}\times(\pi\mathcal{V})^{-1}\omega(e^{\hbar\omega/kT}-1)\times\text{Im}\text{Tr}\{X(\omega-\mathbf{L})^{-1}\rho X\}. \quad (1\text{a})$$

By the resolvent $(\omega-\mathbf{L})^{-1}$ we mean $(\omega+i\epsilon-\mathbf{L})^{-1}$, where ϵ is a real positive increment, made to vanish in the final expression.

Pressure-broadening theory avoids the formidable task of reckoning with all the degrees of freedom of the gas. This is achieved by dividing the sample into a large number of small identical cells, or *systems*, and concentrating on a single system, upon which the remaining gas acts as a thermal bath.

As a result, Eq. (1a) is replaced by [see Eq. (F18)]

$$\alpha(\omega)=-\text{const}(\pi\mathcal{V})^{-1}N_s\omega(e^{\hbar\omega/kT}-1)\times\text{Im}\text{Tr}_{(s)}\left\{X^{(s)}\frac{1}{\omega-\mathbf{L}^{(s)}-\langle\mathbf{M}_c(\omega)\rangle}\rho^{(s)}X^{(s)}\right\}, \quad (2)$$

where N_s is the number of "systems" in the sample, and the label (s) signifies the system subspace. A single system may be, in principle, of any size; i.e., of any number of individual molecules each. In the usual case, such as the one dealt with explicitly in Ref. 4, the system particles consist of one molecule each. In this case N_s is the number of molecules of the absorbing kind, and $\alpha(\omega)$ is proportional to the density $N_s/\mathcal{V}$. The operators $\mathbf{M}$ and $\mathbf{M}_c$ of Ref. 4 [Eqs. (F32) and (F33)] are then defined, with L_i [Eq. (F39)] representing the interaction between a *single* system molecule and a bath molecule, and expanded in power series of the bath density.

However, by such a restriction we exclude an increasingly large body of experimental data usually referred to as *induced spectra*,[10] in which the energy levels and multipole moments of combined pairs of molecules are involved. A considerable part of these spectra arises from metastable states of the pair (i.e., from a continuous energy spectrum with resonance structure) whose lifetime is an intrinsic property of the pair. We therefore may encounter "lines" whose integrated intensity varies as the square of the gas pressure (or product of partial pressures with heterogeneous pairs) while their apparent width is, to the first approximation, independent of the pressure.[11]

---

[8] A. Ben-Reuven, Phys. Rev. Letters 14, 349 (1965).

[9] A. Ben-Reuven (to be published).

[10] H. L. Welsh and J. L. Hunt, J. Quant. Spectry. Radiative Transfer 3, 385 (1963); B. Vodar and H. Vu, *ibid.* 3, 397 (1963); S. Bratož and M. L. Martin, J. Chem. Phys. 42, 1051 (1965); and references thereof.

[11] D. H. Rank, B. S. Rao, and T. A. Wiggins, J. Chem. Phys. 37, 2511 (1962).

There is actually no need to restrict the size of the system particles; in case the intensity includes terms proportional to the nth power of the density it is necessary to consider systems of n molecules each. One should notice, however, that all terms with lower powers of the density are included in this level of approximation.

In writing down Eq. (2) we have not considered the cases in which the resolvent operator connects excitations of one system (s) with another (s'), i.e., terms of the type

$$\mathrm{Tr}\{X^{(s')}(\omega-\mathbf{L})^{-1}\rho^{(s)}X^{(s)}\}$$

which may not vanish. Their contribution, however, is proportional to $N_s\times N_{s'}$ and therefore constitutes a part of a higher order approximation in which both (s) and (s') form parts of a larger single system.

The sole condition for using (2), with a given system size, is the unimportance of spatial correlations between the system and the bath. Under this condition the density matrix may be expressed as the product

$$\rho\approx\rho^{(s)}\times\rho^{(b)}, \tag{3}$$

where (s) and (b) denote system and bath subspaces, respectively. ρ always appears in expressions in which a summation over all bath variables is made. Therefore, the error introduced by this assumption depends on an *average* measure of the interaction, which may be small even if in certain occasions the correlations are quite strong.

In order to facilitate the summation over the bath variables it is necessary to separate them from the system variables by using the product representation

$$|s,b\rangle=|s\rangle\times|b\rangle. \tag{4}$$

A difficulty may arise in the case of *self-broadening*, where the (anti-) symmetrized wave functions of the identical gas molecules should be considered. This difficulty may be removed by the introduction of exchange forces. If, for example, we deal with the low-pressure approximation, in which single "system" and "bath" molecules interact at a time, then we may substitute $V(1\pm F)$ for the binary interaction operator V. F is the exchange operator

$$F|a\rangle|b\rangle=|b\rangle|a\rangle$$

in the two-molecule subspace, and the minus (plus) sign is to be used with molecules obeying Fermi (Bose) statistics. By doing so, the nonsymmetrized product representation (4) may be used, and the distinction between system and bath may be formally carried on.[12]

By a formal extension of the definition of $t(E)$ and $\mathbf{m}(\omega)$ to system particles of any number of molecules, we may generalize Fano's results to any approximation. However, the results of the following sections hardly depend on the specification of the approximation and are generally applicable, unless otherwise stated.

3. IRREDUCIBLE REPRESENTATIONS IN LIOUVILLE SPACE

The Liouville operator $\mathbf{L}$ of a stationary system with a Hamiltonian H is defined as the "operator operating on operators"

$$\mathbf{L}Y\equiv HY-YH, \tag{5}$$

where Y is any ordinary operator in the wave-vector Hilbert space of the system. Thus, $\mathbf{L}$ defines a Hilbert space whose basis vectors are operators in the ordinary wave-vector space of quantum mechanics.[5] Let $|i\rangle$, $|f\rangle$, etc., be eigenvectors of H. Then the operators $|i\rangle\langle f|$ created from the column vectors $|i\rangle$ and the row vectors $\langle f|$ will form eigenvectors of $\mathbf{L}$ since, by (5),

$$\mathbf{L}|i\rangle\langle f|=(E_i-E_f)|i\rangle\langle f|, \tag{6}$$

with the resonance frequencies

$$\omega_{if}=E_i-E_f$$

as eigenvalues. The Hilbert space of operators $|i\rangle\langle f|$, etc., is called the Liouville space.

Suppose, now, the vectors $|i\rangle$, $|f\rangle$, etc., form a basis for the irreducible representations of the symmetry group of H. The vectors $|i\rangle\langle f|$ in Liouville space are products of invariant sets, and a unitary transformation may be required to construct from them a basis for the irreducible representations of the same symmetry group in Liouville space.

More specifically, consider invariance under space rotations, which applies to systems in an isotropic environment. The basis vectors for the irreducible representations in wave-vector space are $|\alpha jm\rangle$, where j is the total angular momentum, m is its projection on a space-fixed axis, and α is a shorthand for all other quantum numbers. The set of $(2j+1)$ bra vectors $\langle\alpha jm|$ $(m=-j,\,-j+1,\,\cdots,\,j)$, is contragredient to the set of ket vectors $|\alpha jm\rangle$[13]; i.e., the latter set transforms like the spherical harmonics Y_{jm} under rotations, whereas the former transforms like $Y_{jm}^*=(-1)^mY_{j-m}$. The invariant subspaces of Liouville space are therefore formed by vector coupling, with $|\alpha_fj_fm_f\rangle$ first transformed to its contragredient set. The invariant sets of order $(2K+1)$ are[14]

$$\begin{aligned}\{|\alpha_ij_i\rangle\langle\alpha_fj_f|\}_Q{}^K&=\sum_{m_im_f}(-1)^{j_f-m_f}C(j_ij_fK;\,m_i-m_fQ)\\&\qquad\times|\alpha_ij_im_i\rangle\langle\alpha_fj_fm_f|.\end{aligned} \tag{7}$$

K may take any integral value from $|j_i-j_f|$ to j_i+j_f.

---

[12] This idea underlies a recent article by A. di Giacomo, Nuovo Cimento 34, 473 (1964).

[13] See U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

[14] See Ref. 13. The extra sign $(-1)^{j_f}$ is introduced to conform to standard phase conventions.

We formally symbolize this coupling scheme by the vector equation

$$\mathbf{j}_i - \mathbf{j}_f = \mathbf{K}. \tag{8}$$

One should distinguish, though, between this coupling and ordinary coupling schemes involving angular momenta of different particles, or different degrees of freedom.

We shall find it convenient to use a notation for Louiville-space vectors suggested by Baranger,[2] i.e.,

$$|a\rangle\langle b| = |ab^+\rangle\rangle \tag{9}$$

by which Eq. (7) can be written as

$$\begin{aligned}|\boldsymbol{\alpha}_i j_i(\boldsymbol{\alpha}_f j_f)^+; KQ\rangle\rangle &= \sum_{m_i m_f} (-1)^{j_f - m_f} C(j_i j_f K; m_i - m_f Q) \\ &\quad \times |\boldsymbol{\alpha}_i j_i m_i(\boldsymbol{\alpha}_f j_f m_f)^+\rangle\rangle. \end{aligned} \tag{7a}$$

Noting that the transformation coefficients are real, we can write down the conjugate vectors

$$\begin{aligned}\langle\langle\boldsymbol{\alpha}_i j_i(\boldsymbol{\alpha}_f j_f)^+; KQ| &= \sum_{m_i m_f} (-1)^{j_f - m_f} C(j_i j_f K; m_i - m_f Q) \\ &\quad \times \langle\langle\boldsymbol{\alpha}_i j_i m_i(\boldsymbol{\alpha}_f j_f m_f)^+|. \end{aligned} \tag{7b}$$

It should be realized, however, that whereas in wave-vector space we distinguish between vectors of different spaces—column vectors $|i\rangle$ and row vectors $\langle f|$—in Liouville space the Hermitian conjugate $|f\rangle\langle i|$ of $|i\rangle\langle f|$ is just another vector of the same space (see Sec. 5).

The Liouville operator of an isolated system is $(2j_i+1)(2j_f+1)$-fold degenerate and diagonal in both the reducible and irreducible representations, with the eigenvalue ω_{if}, for a given pair of energy levels. As will be shown in the following section, however, perturbations may be added which are invariant under rotations, but are not diagonal in j_i and j_f. There the advantage of the K, Q representation is obvious.

The preceding arguments may be extended to other symmetries—e.g., parity. If the vectors $|i\rangle$, $|f\rangle$ have parities π_i, π_f, respectively, $(\pi = \pm 1)$ under inversion of the coordinates, then the Liouville-space vectors will also be eigenvectors of the inversion operator, with eigenvalues

$$\Pi = \pi_i \times \pi_f. \tag{10}$$

Equation (7) may be extended to include parity by just adding the labels π_i, π_f, Π, with Π obeying (10).

A photon state of frequency ω can be identified by the quantum numbers Π, K, Q, of the rotation-inversion group. A photon in this state interacts with the molecular system through the corresponding multipole operator $X^{\Pi K}{}_Q$, where K labels the 2^K-pole, with $\Pi = (-1)^K$ for electric multipoles, and $\Pi = (-1)^{K+1}$ for magnetic multipoles.

Since the Liouville-space vectors $|i\rangle\langle f|$ form a complete basis in a Hilbert space of ordinary *operators*, any such operator Y can be expanded in them,

$$Y = \sum_{ab} |a\rangle\langle a|Y|b\rangle\langle b| = \sum_{ab} Y_{ab} |ab^+\rangle\rangle, \tag{11}$$

by using the closure relation

$$\sum_a |a\rangle\langle a| = 1.$$

A multipole operator $X^{\Pi K}{}_Q$, in particular, may be expanded in terms of the vectors $|\alpha_i \pi_i j_i m_i(\alpha_f \pi_f j_f m_f)^+\rangle\rangle$ of the system. However, since it transforms like an irreducible tensorial set of order $(2K+1)$ with parity Π, it will be composed solely of vectors belonging to the Π,K invariant subspace (the Wigner-Eckart theorem), i.e.,

$$\begin{aligned}X^{\Pi K}{}_Q &= \sum_{\alpha\pi j} \langle \alpha_i \pi_i j_i || X^{\Pi K} || \alpha_f \pi_f j_f\rangle (2K+1)^{-1/2} \\ &\quad \times |\alpha_i \pi_i j_i(\alpha_f \pi_f j_f)^+; \Pi K Q\rangle\rangle, \end{aligned} \tag{12}$$

with coefficients independent of Q. The factor $(2K+1)^{-1/2}$ was introduced to make the remaining factors identical with the *reduced matrix elements* of X, as defined in Ref. 13.[15]

The formal structure presented above corresponds closely to the classical theory where radiation is emitted or absorbed by a set of harmonic oscillators. If we associate the "displacement" of the oscillator with a vector in Liouville space, then the dynamics of the classical system resembles that of the quantum-mechanical system, where the counterpart of the classical normal modes are the Liouville-space basis vectors, the normal frequencies are the eigenvalues of the Liouville operator, and the amplitudes correspond to the (reduced) matrix elements of the multipole operators. Classical terms, like "resonance," "damped oscillations," "harmonics," etc., retain their literal meaning.

4. REDUCTION OF THE RELAXATION MATRIX

So far we have dealt with the invariance properties of eigenvectors in the Liouville space of a stationary system. We now shift our attention to interactions of the system with a thermal bath represented, after averaging over the bath variables, by the relaxation matrix $\langle \mathbf{M}_c \rangle$ which operates on the system variables.

Consider the total Hamiltonian for a pair of "system" and "bath" particles

$$H = H_s + H_b + V, \tag{13}$$

where the interaction V, like H_s and H_b, is invariant under rotation of the coordinates. The transition matrix $t(E)$ for pair collisions is likewise invariant, i.e., it is

---

[15] See Eq. (14.17) of Ref. 13. This definition of the reduced matrix elements differs from the one adopted by various other authors by a factor $(2j_i+1)^{1/2}$ [cf. M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957)].

diagonal in the total angular momentum

$$\mathbf{J}=\mathbf{j}+\mathbf{l} \tag{14}$$

of the pair (where l is the angular momentum of the bath particle, including its motion relative to the system), but not necessarily in j or l. A Liouville vector for the pair

$$|(j_i l_i)J_i M_i[(j_f l_f)J_f M_f]^+\rangle\rangle \tag{15}$$

is obtained by coupling j and l in both levels, using ordinary vector coupling methods. Since $\mathbf{M}(\omega)$ is built out of products of pairs of t matrices—one for each level—it will be diagonal in J_i and J_f, and therefore also in

$$\mathbf{K}=\mathbf{J}_i-\mathbf{J}_f \tag{16}$$

whose eigenvectors

$$|(j_i l_i)J_i[(j_f l_f)J_f]^+;KQ\rangle\rangle \tag{17}$$

are obtained from (15) by a transformation similar to (7).

We can use now Racah recoupling methods to transform to the coupling scheme

$$\mathbf{K}_s=\mathbf{j}_i-\mathbf{j}_f;\ \mathbf{K}_b=\mathbf{l}_i-\mathbf{l}_f;\ \mathbf{K}=\mathbf{K}_s+\mathbf{K}_b, \tag{18}$$

where the irreducible Liouville representations of the system and bath subspaces are first constructed separately and then coupled to K. The transformation of (17) is given by

$$\begin{aligned}|(j_i j_f^+)K_s;\ (l_i l_f^+)K_b;\ KQ\rangle\rangle &=\sum_{J_iJ_f}[(2J_i+1)(2J_f+1)(2K_s+1)(2K_b+1)]^{1/2}\\ &\times\begin{pmatrix} j_i & l_i & J_i\\ j_f & l_f & J_f\\ K_s & K_b & K\end{pmatrix}|(j_i l_i)J_i[(j_f l_f)J_f]^+;KQ\rangle\rangle,\end{aligned} \tag{19}$$

using the Wigner 9-j symbols.[13]

$\mathbf{M}(\omega)$, in general, is *not* diagonal in K_s or K_b, and a change in them signifies the transfer of a resonance excitation (i.e., a photon) from the system to the bath, or vice versa. In forming the average over bath variables $\langle\mathbf{M}\rangle$, however, we consider only matrix elements of $\mathbf{M}$ connecting the Liouville vectors $|\rho^{(s)}X^{(s)},\rho^{(b)}\rangle\rangle$ and $\langle\langle X^{(s)},1^{(b)}|$ (where by $1^{(b)}$ we mean the unit operator in the bath subspace). But, in an *isotropic environment*, $\rho^{(b)}$ is spherically symmetric, and therefore both vectors belong to the invariant subspace $K_b=0$ of the bath variables. Since $\mathbf{M}(\omega)$ is diagonal in K, $\langle\mathbf{M}(\omega)\rangle$ must therefore be diagonal in K_s which can only be equal to K. Equation (19) reduces then to the simpler form

$$\begin{aligned}|(j_i j_f^+)K,(ll^+)0;\ KQ\rangle\rangle &=\sum_{J_iJ_f}(-1)^{j_i+J_f+l+K}(2l+1)^{-1/2}[(2J_i+1)(2J_f+1)]^{1/2}\\ &\times\begin{pmatrix} J_i & J_f & K\\ j_f & j_i & l\end{pmatrix}|(j_i l)J_i[(j_f l)J_f]^+;KQ\rangle\rangle,\end{aligned} \tag{20}$$

using the 6-j symbols.

The above result is readily derived for the relaxation matrix $\langle\mathbf{M}_c\rangle$, since it can be expressed in power series of $\langle\mathbf{M}\rangle$ with only invariant quantities appearing in the coefficients.[16] We have failed so far to mention inversion symmetry, but its inclusion is trivial. If the bath density is invariant under inversion, then $\langle\mathbf{M}_c\rangle$ will also be diagonal in Π. We may thus write down

$$\begin{aligned}&\langle\langle\alpha_i'\pi_i'j_i'(\alpha_f'\pi_f'j_f')^+,\Pi'K'Q'|\\ &\qquad\times\langle\mathbf{M}_c\rangle|\alpha_i\pi_i j_i(\alpha_f\pi_f j_f)^+;\ \Pi KQ\rangle\rangle\\ &=\langle\langle\alpha_i'\pi_i'j_i'(\alpha_f'\pi_f'j_f')^+|\\ &\qquad\times\langle\mathbf{M}_c\rangle^{(\Pi K)}|\alpha_i\pi_i j_i(\alpha_f\pi_f j_f)^+\rangle\rangle\delta_{\Pi\Pi'}\delta_{KK'}\delta_{QQ'}.\end{aligned} \tag{21}$$

The matrix $\langle\mathbf{M}_c\rangle$ is thus reduced to separate submatrices for the various irreducible representations Π, K, each repeated $(2K+1)$ times. The only restricting condition is the requirement that all three terms of H in (13) be invariant under rotations and inversion. This condition is generally achieved in gases in an isotropic environment (i.e., in the absence of external force fields other than the applied radiation field).

It is appropriate to mention that the invariance of the relaxation matrix has been conjectured before, though not proved, and that its reduced form in case of electric dipole radiation ($\Pi=-1$, $K=1$) was explicitly given.[2]

The invariant subspace Π,K in Liouville space is associated with the interaction with a photon of the multipole species Π,K. We are therefore led to the following conclusions concerning isotropic gases:

(a) *Lines belonging to different multipole species never interfere with each other because of collisions.* If the same line is excited by several multipole selection rules, it can be considered a superposition of distinct lines belonging to a different multipole each, with distinct pressure broadening effects. Thus, a line which arises from, say, electric quadrupole and magnetic dipole transitions, will behave as two distinct lines, with different shifts and widths, though their unperturbed frequencies are identical. This effect should be observable in principle (provided, of course, the intensities of the two components are not drastically different).

(b) The relaxation matrix is independent of Q. Hence *the shape of the spectrum is independent of the polarization of the photon*, specified by Q. We may completely avoid the use of Q in the calculation of (2) by using (21). With the reduced-matrix elements of $X^{\Pi K}$, as defined in (12), the trace in (2) can be written as

$$\begin{aligned}&(2K+1)^{-1}\sum_{ii'ff'}\langle f'||X^{\Pi K}||i'\rangle\\ &\qquad\times\langle\langle i'f'^+|[\omega-\mathbf{L}^{(s)}-\langle\mathbf{M}_c\rangle^{(\Pi K)}]^{-1}|if^+\rangle\rangle\\ &\qquad\qquad\times\langle i||X^{\Pi K}||f\rangle\rho_i\end{aligned} \tag{22}$$

with $\langle\mathbf{M}_c\rangle$ in the reduced representation (21). Here i, f are shorthand for all the system's quantum numbers, *not* including magnetic numbers; $\rho_i=Z^{-1}\exp(-\beta E_i)$

---

[16] See Eq. (20) of Ref. 4.

in the energy representation (where $\beta=\hbar/kT$, and Z is the partition function).

Though we have dealt explicitly with emission or absorption spectra, the above conclusions hold in any problem which deals with linear effects of the interaction of photons with isotropic gases, where the relaxation matrix $\langle\mathbf{M}_c\rangle$ is involved. These cases include Raman (and Rayleigh) scattering of light,[17] and dispersion of light [which involves the real part of the trace in (2)].

The real and imaginary parts of a diagonal matrix element of $\langle\mathbf{M}_c\rangle$ describe the shift and the width of the corresponding line, provided it is well separated from other lines of the same multipole species. It is remarkable that the damping of a line (i.e., its pressure broadening) is given in terms of matrix elements of $\mathbf{M}$ diagonal in K_s, whereas the relaxation process involves the transfer of a photon from the system to the bath. This implies that matrix elements of $\mathbf{M}(\omega)$ are not completely independent of each other and that matrix elements diagonal in K_s include information concerning off-diagonal elements. This resembles the situation in wave-vector space, where the forward scattering amplitude is related to the total scattering cross section by the optical theorem. The idea of an "optical theorem" in Liouville space is imbedded in Eq. (37b) of Ref. 4.

5. LIOUVILLE-CONJUGATE PAIRS

Let $|i\rangle$, $|f\rangle$, etc., form a complete set of orthonormal wave vectors. The set of operators $|i\rangle\langle f|$ is not, in general, Hermitian, and both $|i\rangle\langle f|$ and its Hermitian conjugate $|f\rangle\langle i|$ form distinct eigenvectors in Liouville space, with opposite eigenvalues $\omega_{if}=-\omega_{fi}$. (The only exceptions are the self-conjugate vectors $i=f$, with eigenvalues $\omega_{ii}=0$.) We define an operation in Liouville space "reflecting" $|i\rangle\langle f|$ into $|f\rangle\langle i|$ and vice versa,

$$|f\rangle\langle i|=\mathbf{C}_L|i\rangle\langle f|,\quad(\mathbf{C}_L^{-1}=\mathbf{C}_L),\tag{23}$$

and call it *Liouville conjugation*. The Liouville-conjugate operator to any operator $\mathbf{A}$ in Liouville space is defined by

$$\langle\langle ab^{+}|\mathbf{C}_L\mathbf{A}\mathbf{C}_L|a'b'^{+}\rangle\rangle=\langle\langle ba^{+}|\mathbf{A}|b'a'^{+}\rangle\rangle\tag{24}$$

and should be distinguished from *Hermitian conjugation* in Liouville space, defined by

$$\langle\langle ab^{+}|\mathbf{A}^{\dagger}|a'b'^{+}\rangle\rangle=\langle\langle a'b'^{+}|\mathbf{A}|ab^{+}\rangle\rangle^{*},\tag{25}$$

where the asterisk denotes complex conjugation. The existence of such two distinct operations should not surprise us, remembering that A is a tetradic, and not a dyadic, in wave function representation.

The Liouville vector $|i\rangle\langle f|$ is usually associated with a physical process in which a transition occurs from state i to state f, while $|f\rangle\langle i|$ is associated with the inverse transition $f\rightarrow i$. Liouville conjugation is therefore closely related to *time reversal*.[18] In an elementary physical process (i.e., a Feynman diagram) Liouville conjugation describes the reversal in the temporal sequence of states (lines) in the diagram, whereas the ordinary time reversal operation of quantum mechanics describes the changes in each state necessary to construct the time-reversed solution of the Schrödinger equation.

In this section we study the relation of the relaxation matrix to its Liouville conjugate, and its further simplification which results from this relation.

Consider one of the definitions of the operator $\mathbf{M}(\omega)$ [Eqs. (F14*a*)], say, the series expansion

$$\mathbf{M}(\omega)=\mathbf{L}_1+\sum_{n=0}^{\infty}\mathbf{L}_1\left(\frac{1}{\omega-\mathbf{L}_0}\mathbf{L}_1\right)^{n}.\tag{26}$$

Both $\mathbf{L}_0$ and $\mathbf{L}_1$ are defined by an equation of the type (5), with H Hermitian. Therefore, both obey

$$\langle\langle\beta\alpha^{+}|\mathbf{L}|ba^{+}\rangle\rangle=-\langle\langle\alpha\beta^{+}|\mathbf{L}|ab^{+}\rangle\rangle^{*},\tag{27}$$

or, in operator notation,

$$\mathbf{C}_L\mathbf{L}\mathbf{C}_L=-\mathbf{L}^{*}\tag{27a}$$

(where the asterisk denotes complex conjugation of the elements of a matrix). Notice also that

$$\mathbf{C}_L(\omega-\mathbf{L}_0)^{-1}\mathbf{C}_L=-[(-\omega^{*}-\mathbf{L}_0)^{-1}]^{*}.\tag{28}$$

Each term in the series (26) is a product of an odd number of operators each obeying either (27) or (28). Therefore,

$$\mathbf{C}_L\mathbf{M}(\omega)\mathbf{C}_L=-\mathbf{M}^{*}(-\omega^{*}).\tag{29}$$

In the process $\langle\cdots\rangle$ of averaging over bath variables [Eq. (F17)] we pick up only the set of self-conjugate vectors $|bb^{+}\rangle\rangle$ in the bath subspace, in which $\mathbf{C}_L$ is diagonal. Therefore the Liouville conjugation commutes with $\langle\cdots\rangle$. Furthermore, only its part $\mathbf{C}_L^{(s)}$ in the system subspace should be considered after the averaging. The averaging process is a real operation, and therefore

$$\mathbf{C}_L^{(s)}\langle\mathbf{M}(\omega)\rangle\mathbf{C}_L^{(s)}=-\langle\mathbf{M}(-\omega^{*})\rangle^{*}.\tag{30}$$

Finally, since $\langle\mathbf{M}_c\rangle$ can be expressed as a power series of $\langle\mathbf{M}\rangle$ [Eq. (F20)], with the coefficients $(\omega-\mathbf{L}^{(s)})^{-1}$ obeying Eq. (28) in the system subspace, we get

$$\mathbf{C}_L^{(s)}\langle\mathbf{M}_c(\omega)\rangle\mathbf{C}_L^{(s)}=-\langle\mathbf{M}_c(-\omega^{*})\rangle^{*}\tag{31}$$

for the relaxation matrix.

$\langle\mathbf{M}_c(\omega)\rangle$ may be written as a sum of two matrices, one an even and one an odd function of the real part of

---

[17] J. Fiutak and J. Van Kranendonk, Can. J. Phys. **40**, 1085 (1962); J. Fiutak, Acta Phys. Polon. **26**, 919 (1964).

[18] The equivalent relation to time reversal in classical mechanics has been pointed out by I. Prigogine, in his book *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, New York, 1962), p. 20.

ω, to be denoted as $\langle\mathbf{M}_c^+(\omega)\rangle$ and $\langle\mathbf{M}_c^-(\omega)\rangle$, respectively. Then

$$\mathbf{C}_L^{(s)}\langle\mathbf{M}_c^{\pm}(\omega)\rangle\mathbf{C}_L^{(s)}=\mp\langle\mathbf{M}_c^{\pm}(\omega)\rangle^*. \tag{31a}$$

Equation (31) may be helpful in further simplifying the relaxation matrix, particularly in the impact approximation (or approximation of Markoffian collisions), in which the dependence of $\langle\mathbf{M}_c(\omega)\rangle$ on the frequency is negligible in the finite range of frequencies under consideration.[19]

If the range of frequencies in which the impact approximation is valid is larger than $2\omega_{if}$, we may write

$$\langle\mathbf{M}_c(\omega)\rangle\approx\langle\mathbf{M}_c^+(0)\rangle=\Lambda=\Delta-i\Gamma, \tag{32}$$

where both Δ and Γ are Hermitian. From (31a) we have

$$\begin{aligned}\langle\langle fi^+|\Delta|fi^+\rangle\rangle&=-\langle\langle if^+|\Delta|if^+\rangle\rangle=-\delta_{if},\\ \langle\langle fi^+|\Gamma|fi^+\rangle\rangle&=\langle\langle if^+|\Gamma|if^+\rangle\rangle=\gamma_{if},\end{aligned} \tag{33}$$

where the real parameters δ_{if} and γ_{if} are, respectively, the *shift* and the *width* of the line $i\rightarrow f$ (in the absence of other neighboring lines). The broadening of the line, expressed by γ, contributes to the line shape at frequencies ω off the resonance ω_{if} and (neglecting for a moment all the off-diagonal elements of Λ) results in the Lorentzian term $\gamma[\gamma^2+(\omega-\omega_{if}-\delta_{if})^2]^{-1}$ in $\alpha(\omega)$. But the transition $f\rightarrow i$, with resonance frequency $-\omega_{if}$, will also contribute to the line shape if γ is not small compared to ω_{if}; the resulting term

$$\gamma[\gamma^2+(\omega+\omega_{if}+\delta_{if})^2]^{-1}$$

is the familiar "negative resonance" term in the shape of low-frequency (radio and microwave) spectra.[20] Equation (33) tells us that the "positive resonance" and "negative resonance" terms have equal widths and opposite shifts.

Consider now the off-diagonal elements of Λ combining the two conjugate modes. From (31a) we find that

$$\langle\langle if^+|\Delta|fi^+\rangle\rangle=\langle\langle fi^+|\Delta|if^+\rangle\rangle=0, \tag{34}$$

i.e., in the impact approximation, the part of $\langle\mathbf{M}_c\rangle$ combining the two conjugate modes is anti-Hermitian. These matrix elements are composed of sums of the product of transition amplitudes $t_{if}t_{fi}^*$ and become important in low-frequency spectra where the two levels i, f are close enough to make transitions from the one to the other by inelastic collisions quite probable. These off-diagonal elements have, therefore, a considerable effect on the shape of lines in these spectral regions.[8,9]

We shall finally mention the particular case of the self-conjugate vectors $|ii^+\rangle\rangle$. These will also give rise to absorption spectra when broadened, though their resonance frequency is zero; such spectra are familiar by the name of *nonresonant* (or Debye) spectra.[21] By (31a)

$$\langle\langle ii^+|\Delta|ii^+\rangle\rangle=0, \tag{35}$$

i.e., in this case the spectrum will be only broadened without altering its zero resonance frequency.

Nonresonant spectra may also arise from transitions $i\rightarrow f$ where i and f are degenerate though distinct states. The two Liouville vectors $|if^+\rangle\rangle$ and $|fi^+\rangle\rangle$ are conjugate to one another rather than self-conjugate. However, since they are degenerate eigenvectors of $\mathbf{L}^{(s)}$, they may be transformed to a pair of self-conjugate eigenvectors,

$$\begin{aligned}|\alpha\rangle\rangle&=\frac{1}{\sqrt{2}}\{|if^+\rangle\rangle+|fi^+\rangle\rangle\},\\ |\beta\rangle\rangle&=\frac{i}{\sqrt{2}}\{|if^+\rangle\rangle-|fi^+\rangle\rangle\}.\end{aligned} \tag{36}$$

Then

$$\langle\langle\alpha|\Delta|\alpha\rangle\rangle=\langle\langle\beta|\Delta|\beta\rangle\rangle=0. \tag{35a}$$

Since Liouville conjugation of a vector in Liouville space is equivalent, by definition, to Hermitian conjugation of an operator in wave-vector space, (36) is the familiar rule for constructing two Hermitian operators out of a non-Hermitian operator and its Hermitian conjugate. The imaginary unit i in the second Eq. (36) reflects the antilinear character of $\mathbf{C}_L$.

Equations (33) through (35) examplify the application of Eq. (31). Further applications will be illustrated in Ref. 9.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. U. Fano for his continuous encouragement and support in the course of this work, and to Dr. A. A. Maryott for discussions of the manuscript. Thanks are also due to Dr. H. Friedmann for helpful comments.

---

[19] See Refs. 2 and 4. This is a further simplification of the low-pressure approximation in which both system and bath particles consist of one molecule each. The relaxation matrix is practically independent of ω in a range of frequencies $\Delta\omega$ comparable to the inverse average duration of a collision (which is several wave numbers wide in typical cases, involving light molecules at room temperatures). Therefore the impact approximation is valid in a range of frequencies larger than $2\omega_{if}$ in many microwave spectra.

[20] See, e.g., R. de L. Kronig, Physica **5**, 65 (1938); J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945); H. Fröhlich, Nature **157**, 478 (1946).

[21] See, e.g., J. H. Van Vleck, Phys. Rev. **71**, 413 (1947); J. E. Walter and W. D. Hershberger, J. Appl. Phys. **17**, 814 (1946); G. Birnbaum, J. Chem. Phys. **27**, 360 (1957).