Another possibility is to use the generator-coordinate method to treat the interaction between various collective modes as suggested in Refs. 22 and 6. Last but not least, the Feynman[23] and Feynman-Cohen[24] approach to liquid helium is easily seen to fall within the formalism of the generator-coordinate method if one identifies the generator coordinates with the coordinates of the atoms in the liquid.

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Nonlinear Optical Polarization and Relaxation Phenomena in Dilute Gases

Abraham Ben-Reuven
Department of Electronics, The Weizmann Institute of Science, Rehovot, Israel

and

Lewis Klein*†
Department of Physics, Howard University, Washington, D.C. 20001

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The Kubo-Zwanzig-Fano relaxation method is extended to the problem of a homogeneous dilute system interacting with arbitrarily strong fields composed of several monochromatic modes, neglecting breakdown and spatial correlations. The Von Neumann equation for the density matrix is solved for classical fields, using a procedure in which the harmonics numbers are treated as the classical analog (in Liouville space) of the quantum fields occupation-number representation. This solution is adapted to the case where memory effects during the absorption or emission of a photon can be neglected. Two examples illustrate the method, which is generally applicable in such problems as saturation, double resonance, and frequency mixing involving the nonlinear response of independent molecules.

I. INTRODUCTION

The understanding of relaxation phenomena in resonance spectra of gases and other dilute systems in the linear-response approximation has been improved considerably by the introduction of operator techniques[1,2] and quantum-field-theoretic methods.[3,4] Little has been done, however, in using these methods in the domain of nonlinear optics. The method of Liouville operators developed by Fano[2] has been applied by Lambropoulos[5] to the problem of radiation damping combined with pressure broadening. A formal introduction of Liouville-operator methods to nonlinear optics, with quantum fields, has been worked out by Agarwal.[6]

Our aim here is to introduce methods of linear-response theory to the nonlinear response of resonant dilute media. The practical goal is to connect the formal approach to the phenomenological description of collision-broadening effects in nonlinear optics, such as is usually encountered in works on saturation,[7,8] frequency mixing,[9] and double resonance.[8,10,11] With proper modifications the methods described here may be extended to such problems as the effect of pressure on the output power of lasers.[12,13]

Several major assumptions restrict the scope of this work. We neglect multiphoton processes of transfer of excitation from one molecule to another, as in radiation trapping, and consider only nonlinear response by single molecules. For that matter, we also restrict the discussion to temporal correlations, avoiding spatial effects such as in self-focusing. The molecules are treated as stable entities, disregarding breakdown or ionization phenomena. It is also assumed that the incident radiation field is itself unaffected by the medium, and that it can be treated as a classical field for most practical purposes. For these reasons our work deals mainly with gases undergoing interaction with strong optical, infrared, or microwave radiation, though with some modifications it can be applied to other dilute systems, such as dilute solutions or impurities in a solid matrix. It can also be used with appropriate reformulation in problems involving paramagnetic resonance, magnetoelectric phenomena, etc. The discussion in the form given here is limited to a single particle (the molecule) undergoing relaxation while resonating with one, or several, strong monochromatic fields.

The work opens with a general introduction to the Liouville-operator technique and its application to the nonlinear response of a gas in a classical field composed of several monochromatic fields. For the derivation of a Dyson-type equation, the harmonics-number representation is introduced, in analogy with the quantum field occupation-number representation. The application of the occupation-number methods to classical fields is permitted in the Liouville-space formalism, where the equations of motion for classical and for quantum systems are similar.[1] The gap between the formal theory and the phenomenological treatment of resonance lines is bridged by the introduction of a short-memory approximation and the impact approximation of collision-broadening theory.[14] Finally a simple diagrammatic method is presented for calculating nonlinear polarizations with arbitrarily strong fields. This method is illustrated by two examples: (1) the saturation of a resonance line (the two-level problem) including inelastic collisions between the levels; and (2) the linear response to a weak field in the presence of a strong monochromatic field, with both fields at near resonance with a molecular transition. These diagrammatic methods can be extended to other problems involving more than two levels and (or) several monochromatic fields.

II. NONLINEAR RESPONSE

Consider a dilute molecular sample with a dipole moment $\vec{\mu}$ introduced into an alternating classical electric field $\vec{E}(t)$. In the absence of the field, the sample is assumed to be in equilibrium, obeying the Liouville equation

$$i\frac{\partial}{\partial t}\rho_e = L\rho_e = 0\ , \tag{1}$$

where ρ_e is the density matrix of the sample, and L is the Liouville operator, or Liouvillian, defined for quantum systems as

$$Lx = \hbar^{-1}[H, x]\ , \tag{2}$$

x being any dynamical variable of the system, and H being the Hamiltonian. Thus L is an operator in the Hilbert space spanned by the dynamical variables x, also known as the Liouville space.[2]

In the presence of the field, the density matrix can be written in the form

$$\rho(t) = \rho_e + \delta\rho(t)\ . \tag{3}$$

Using Eq. (1), the Von Neumann equation for ρ becomes

$$i\frac{\partial}{\partial t}\delta\rho(t) - L\delta\rho(t) = -\vec{M}\cdot\vec{E}(t)[\rho_e + \delta\rho(t)]\ , \tag{4}$$

where

$$M_i x = \hbar^{-1}[\mu_i\,,\ x] \quad (i = x, y \text{ or } z) \tag{5}$$

defines the Liouville-space analog of the dipole moment. The field E is treated as a classical (c-number) quantity. Equation (4) has been written using the electric dipole approximation for the interaction with the field.

Following the method of Kubo,[15] we transform Eq. (4) into an integral equation,

$$\delta\rho(t) = -\int_{-\infty}^{\infty} G(t-t')\vec{M}\cdot\vec{E}(t')[\rho_e + \delta\rho(t')]\,dt'\ , \tag{6}$$

introducing a Green's function defined by the equation

$$i\frac{\partial}{\partial t}G(t) - LG(t) = \delta(t)\ , \tag{7}$$

where $\delta(t)$ is the Dirac δ function. The appropriate Green's function, obeying the causal boundary condition

$$G(t)=0 \quad \text{for } t<0 \tag{8}$$

is

$$G(t)=-i\theta(t)\,e^{-iLt}\ , \tag{9}$$

where $\theta(t)$ is the Heaviside step function. Let

$$F(t)=-\vec{\mathrm{M}}\cdot\vec{\mathrm{E}}(t)[\rho_e+\delta\rho(t)] \tag{10}$$

represent the right-hand side of Eq. (4), and

$$F(\omega)=\int_{-\infty}^{\infty}e^{i\omega t}F(t)\,dt \tag{11}$$

its Fourier transform. Then, by the convolution theorem of Fourier transforms, we get

$$\delta\rho(\omega)=G(\omega)F(\omega)\ , \tag{12}$$

where

$$G(\omega)=[\omega+i\epsilon-L\,]^{-1} \tag{13}$$

is the Fourier transform of $G(t)$. Here the limit $\epsilon\to+0$ is implied.

Application of the convolution theorem to the integral equation (6) leads to

$$\delta\rho(\omega)=-G(\omega)[\vec{\mathrm{M}}\cdot\vec{\mathrm{E}}(\omega)\rho_e + (2\pi)^{-1}\int_{-\infty}^{\infty}\vec{\mathrm{M}}\cdot\vec{\mathrm{E}}(\omega')\delta\rho(\omega-\omega')\,d\omega'\,]\ . \tag{14}$$

This equation is usually solved by iteration, inserting

$$\delta\rho(\omega)=\sum_{j=1}^{\infty}\rho^{(j)}(\omega)\ , \tag{15}$$

which is in fact a series expansion in powers of the applied field. We thus obtain a series of recursion relations

$$\rho^{(j+1)}(\omega)=-(2\pi)^{-1}G(\omega)\int_{-\infty}^{\infty}\vec{\mathrm{M}}\cdot\vec{\mathrm{E}}(\omega')\rho^{(j)}(\omega-\omega')\,d\omega' \qquad (j=1,2\ldots)\ , \tag{16}$$

the first iteration being Kubo's solution for the linear response,

$$\rho^{(1)}(\omega)=-G(\omega)\,\vec{\mathrm{M}}\cdot\vec{\mathrm{E}}(\omega)\rho_e\ . \tag{17}$$

The polarization of the sample at the angular frequency ω is then defined as

$$\vec{\mathrm{p}}(\omega)=V^{-1}\operatorname{tr}[\vec{\mu}\,\delta\rho(\omega)]\ , \tag{18}$$

where V is the volume of the sample, and tr denotes the trace in the ordinary (Schrödinger) sense.

III. MONOCHROMATIC FIELDS

Consider a superposition of several monochromatic fields

$$E(t)=\operatorname{Re}\textstyle\sum_k E_k^{+}\,e^{-i\omega_k t}\ , \tag{19}$$

each mode having a well-defined angular frequency ω_k, amplitude $|E_k^{+}|$, polarization, and phase. We are generally allowed to do so if we confine our sample to a resonance cavity with well-defined modes. The Fourier transform of the field is

$$E(\omega)=\pi\textstyle\sum_k[E_k^{+}\,\delta(\omega-\omega_k)+E_k^{-}\,\delta(\omega+\omega_k)]\ , \tag{20}$$

where E_k^{-} is the c. c. of E_k^{+}.

The polarization $\vec{\mathrm{p}}(\omega)$ is then a sum of δ functions, with contributions from various combinations of harmonics of the fundamental frequencies; i. e.,

$$\vec{\mathrm{n}}\cdot\vec{\omega}=\textstyle\sum_k n_k\omega_k \qquad (n_k=0,\ \pm1,\ \ldots \quad \text{for each } k)\ , \tag{21}$$

where

$$\vec{\mathrm{n}}=(n_1,\ \ldots,\ n_k,\ \ldots) \tag{22}$$

is a set of harmonics numbers, and

$$\vec{\omega}=(\omega_1,\ \ldots,\ \omega_k\ldots) \tag{23}$$

is the set of fundamental frequencies of the field.

A set of algebraic equations can be obtained from the integral equation for $\rho(\omega)$ by setting

$$\begin{aligned}\rho(\omega')&=2\pi\textstyle\sum_{\vec{\mathrm{n}}}R(\vec{\mathrm{n}}\cdot\vec{\omega})\delta(\omega'-\vec{\mathrm{n}}\cdot\vec{\omega})\\&=2\pi\textstyle\sum_k\sum_j R^{(j)}(\vec{\mathrm{n}}\cdot\vec{\omega})\delta(\omega'-\vec{\mathrm{n}}\cdot\vec{\omega})\ .\end{aligned} \tag{24}$$

The iterative equations then become

$$R^{(j)}(\vec{\mathrm{n}}\cdot\vec{\omega})=-\tfrac{1}{2}G(\vec{\mathrm{n}}\cdot\vec{\omega})\textstyle\sum_k\sum_{\pm}M_kE_k^{\pm}R^{(j-1)}(\vec{\mathrm{n}}\cdot\vec{\omega}\mp\omega_k)\ , \tag{25}$$

where M_k is the projection of the vector $\vec{\mathrm{M}}$ along the polarization $\vec{\mathrm{E}}_k$ of the kth mode. The first iteration is

$$R^{(1)}(\pm\omega_k)=-\tfrac{1}{2}G(\pm\omega_k)M_kE_k^{\pm}\rho_e\ . \tag{26}$$

In the calculation of $\vec{\mathrm{p}}(\omega)$ we are interested in *positive* values of ω, as the physically meaningful values. However, *negative* values may appear at intermediate steps in the iteration process, and should not be overlooked.

IV. HARMONICS-NUMBER REPRESENTATION

A solution of the iterative equations in closed form is possible by means of a Dyson-type equation, analogous to the one obtained in quantum field theory. For this purpose we need to introduce a method analogous to the occupation-number representation of quantum field theory. Such an attempt would be meaningless for classical fields if the ordinary Schrödinger equations of motion for the sample were used. It is possible, however, in the Liouville-space representation. The classical analog of the occupation numbers in Liouville space are the harmonics numbers, which count not absolute numbers of photons present in the field but only numbers of photons taken from or added to the field by absorption or emission.

Notice that E_k^{+} and E_k^{-} in Eq. (25) are, respectively, followed by a raising and lowering of the harmonics number n_k by a unit. We can therefore define for the classical field a Liouville-space set of vectors labeled by the harmonics numbers

$$|\vec{n}\rangle\rangle \equiv |n_1, \ldots, n_k, \ldots\rangle\rangle . \tag{27}$$

The double-bracket notation is used to distinguish these vectors from the Dirac vectors in ordinary (Schrödinger) space. We can define now the raising and lowering operators $\mathcal{E}_k^{\pm}$ (to be distinguished from the numbers $E_k^{\pm}$),

$$\mathcal{E}_k^{\pm} |n_1, \ldots, n_k, \ldots\rangle\rangle = E_k^{\pm} |n_1, \ldots, n_k \pm 1, \ldots\rangle\rangle . \tag{28}$$

Since we deal here with a *classical* field, the two operators *commute* with each other.

Our Liouville space is now redefined as the product of the ordinary (quantum) Liouville space of the sample and the harmonics-number (classical) space of the radiation field. All our equations can then be written in terms of this newly defined space, thus transferring all our ω dependence into the occupation-number representation.

For example, we can define the vector $\mathcal{R}$ in this notation, which has $R(\vec{n}\cdot\vec{\omega})$ as its projection on $|\vec{n}\rangle\rangle$, i.e.,

$$\mathcal{R} = \sum_{\vec{n}} R(\vec{n}\cdot\vec{\omega}) \, |\vec{n}\rangle\rangle . \tag{29}$$

Similarly, G can be redefined as an operator diagonal in the $\vec{n}$ states; its diagonal elements are functions of the frequency,

$$\langle\langle \vec{n}' | G | \vec{n}\rangle\rangle = \delta_{\vec{n},\vec{n}'} \, G(\vec{n}\cdot\vec{\omega}) . \tag{30}$$

The iterative equations can now be written in this extended notation as the operator equations

$$\mathcal{R}^{(j)} = GU\mathcal{R}^{(j-1)} \quad (j = 1, 2 \ldots) , \tag{31}$$

where

$$U = -\tfrac{1}{2}\sum_k \sum_{\pm} M_k \mathcal{E}_k^{\pm} . \tag{32}$$

The linear-response approximation is thus

$$\mathcal{R}^{(1)} = GU\mathcal{R}^{(0)} , \tag{33}$$

where

$$\mathcal{R}^{(0)} = \rho_e \, |\vec{0}\rangle\rangle , \tag{34}$$

$|\vec{0}\rangle\rangle$ here being the "vacuum" vector ($\vec{n} = 0$) in our harmonics-number representation.

The series of iterative equations (31) can be combined into a single equation,

$$\mathcal{R} = \mathcal{G} U \mathcal{R}^{(0)} , \tag{35}$$

where $\mathcal{G}$ obeys the Dyson equation

$$\mathcal{G} = G + GU\mathcal{G} . \tag{36}$$

Its formal solution is

$$\mathcal{G} = [G^{-1} - U]^{-1} = [\Omega - L - U + i\epsilon]^{-1} . \tag{37}$$

Here Ω is the diagonal matrix of harmonics frequencies

$$\Omega \, |\vec{n}\rangle\rangle = \vec{n}\cdot\vec{\omega} \, |\vec{n}\rangle\rangle , \tag{38}$$

and the Liouvillian L, in the extended notation, does not operate on the $\vec{n}$ space. We thus can write

$$\begin{aligned} R(\vec{n}\cdot\vec{\omega}) &= \langle\langle \vec{n} | \mathcal{G} U | \vec{0}\rangle\rangle \rho_e \\ &= \langle\langle \vec{n} | [\Omega - L - U + i\epsilon]^{-1} U | \vec{0}\rangle\rangle \rho_e . \end{aligned} \tag{39}$$

The polarization at ω' is given by

$$\vec{p}(\omega') = 2\pi \sum_{\vec{n}} \vec{P}(\vec{n}\cdot\vec{\omega}) \, \delta(\omega' - \vec{n}\cdot\vec{\omega}),$$

where

$$\vec{P}(\vec{n}\cdot\vec{\omega}) = V^{-1} \operatorname{tr}(\vec{\mu} \langle\langle \vec{n} | \mathcal{G} U | \vec{0}\rangle\rangle \rho_e) , \tag{40}$$

or, in our operator notation,

$$\vec{\mathcal{P}} = V^{-1} \operatorname{tr}(\vec{\mu} \, \mathcal{G} U \mathcal{R}^{(0)}) , \tag{41}$$

where

$$\vec{\mathcal{P}} = \sum_{\vec{n}} \vec{P}(\vec{n}\cdot\vec{\omega}) \, |\vec{n}\rangle\rangle , \tag{42}$$

the trace being taken over the sample alone. The linear response is obviously obtained by omitting the perturbation U from the denominator in (39). For the nonlinear response one can expand $\mathcal{G}$ in a power series of U,

$$\mathcal{G} U = GU + GUGU + \cdots . \tag{43}$$

This expansion can be represented by diagrams, with vertices signifying $\vec{n}$ states and lines signifying U, in order to sum the series in particular problems.

Since we deal here explicitly with electric dipole radiation, we can introduce at this stage an additional simplification resulting from parity considerations. Electric dipoles have odd parity while the equilibrium state ρ_e of a gas sample has even parity. We can therefore split the vector $\mathcal{R}$ in our extended Liouville space into an even part and an odd part, decouple the respective equations, and consider only the odd part in the calculation of $\vec{p}(\omega)$. Let

$$\mathcal{R} = D_p \mathcal{R} + (1 - D_p) \mathcal{R} , \tag{44}$$

where D_P is the projection operator for the even part of $\mathcal{R}$. As U is odd in the sample coordinates, let us define a new even perturbation operator

$$W = UGU . \tag{45}$$

Then we can write separate Dyson equations of the type

$$\mathcal{G} = G + GW\mathcal{G} , \tag{46}$$

for the even and odd parts of $\mathcal{R}$. The polarization, which depends only on the odd part of $\mathcal{R}$, may then be written as

$$\vec{\mathcal{P}} = V^{-1}\,\mathrm{tr}[\,\vec{\mu}\,(\Omega - L - W + i\epsilon)^{-1}\, U\mathcal{R}^{(0)}\,]\,. \tag{47}$$

This form has the advantage of reducing by a factor 2 the number of steps in each diagram. Obviously, this cannot be done with magnetic fields.

V. PROJECTION-OPERATOR METHOD

In dilute systems, where we consider the absorption by single molecules, we can express the polarization as a sum of contributions of N individual molecules. We therefore distinguish, following Fano,[2] between the "absorbing system" (the molecular dipole) and the "thermal bath" (the rest of the sample), and average out the bath degrees of freedom using Zwanzig projection operators.

Let

$$|\,\mu_i\,\rangle\rangle = \textstyle\sum_\alpha \mu_{i,\alpha}\,|\,u_\alpha\rangle\rangle \tag{48}$$

be the expansion of the i component of the molecular dipole moment in the subspace of Liouville space corresponding to the absorbing system. Here μ_α is a member of an orthonormal set of unit vectors. For example,

$$|\,u_{ab}\rangle\rangle = |\,ab^{+}\rangle\rangle \tag{49}$$

is the unit vector corresponding to the operator $|\,a\rangle\langle\,b\,|$ in the ordinary (Schrödinger) space of quantum mechanics; $\mu_{i,ab}$ is then the corresponding matrix element of μ_i.

Whenever we deal with an isolated spectral line represented by a single term $\mu_{i,\alpha}u_\alpha$, neglecting all other terms in the absorbing system's subspace, we can define the pair of projection operators

$$D_\alpha = \frac{|\,u_\alpha\rho_e\rangle\rangle\langle\langle u_\alpha\,|}{\langle\langle u_\alpha\,|\,u_\alpha\rho_e\rangle\rangle}\,,$$

$$D'_\alpha = \frac{|\,\rho_e u_\alpha\rangle\rangle\langle\langle u_\alpha\,|}{\langle\langle u_\alpha\,|\,\rho_e u_\alpha\rangle\rangle}\,, \tag{50}$$

where $\langle\langle u_\alpha\,|$ represents the Hermitian conjugate of the operator u_α in Schrödinger space. The "scalar product" in the denominator signifies a trace in Schrödinger space, i.e.,

$$\langle\langle u_\alpha\,|\,u_\beta\rho_e\rangle\rangle \equiv \mathrm{tr}(u_\alpha^{+}u_\beta\rho_e)\,. \tag{51}$$

In particular, using the representation (49) as a basis, we can write

$$\langle\langle u_{ab}\,|\,u_{cd}\rho_e\rangle\rangle = \mathrm{tr}(\,|\,b\rangle\langle d\,|\,\rho_e)\delta_{ac}$$

$$= \langle d\,|\,\rho_S\,|\,b\rangle\,\delta_{ac}\,. \tag{52}$$

Here

$$\rho_S = \mathrm{tr}_B\,\rho_e = \sum_{\text{bath}} \langle\beta\,|\,\rho_e\,|\,\beta\rangle \tag{53}$$

is the trace of ρ_e over the complete set in Schrödinger space, $\{\,|\,\beta\rangle\}$, which covers the bath subspace; i.e., it is a density matrix in the absorbing system's space, obtained by averaging over the bath.

If we wish to consider several resonance lines (a "band") in the Liouville subspace of the absorbing system, we can extend the definition of the projection operators so that

$$D = \textstyle\sum_\alpha D_\alpha\,,\quad D' = \textstyle\sum_\alpha D'_\alpha\,, \tag{54}$$

where the summation is carried over the band of resonance lines.

An approximation of considerable practical importance for dilute gases used by Fano[2] is to assume ρ_e is separable into independent density matrices for the absorbing system and for the thermal bath,

$$\rho_e \simeq \rho_S\,\rho_B\,, \tag{55}$$

where for ρ_S we may choose Eq. (53). Under this approximation we can also split the projection operators,

$$D_\alpha = D_{S\alpha}D_B\,,\quad D = D_S D_B\,, \tag{56}$$

where D_B simply implies an averaging over the bath with ρ_B.

The linear-response polarization (which in nonisotropic media is not necessarily parallel to the applied field) due to a single-field mode k, written in terms of the projection operators, has the ith Cartesian component

$$P_i^{(1)}(\omega_k) = -\tfrac{1}{2}\hbar^{-1}(N/V)\{\langle\langle\mu_i\,|\,DG(\omega_k)D\,|\,\mu_k\rho_e\rangle\rangle$$

$$-\langle\langle\mu_i\,|\,D'\,G(\omega_k)D'\,|\,\rho_e\,\mu_k\rangle\rangle\}E_k^{+}\,. \tag{57}$$

Here μ_k is the projection of the molecular dipole $\vec{\mu}$ along $\vec{\mathrm{E}}_k$, and N/V is the number density of absorbing dipoles. In an isotropic dilute medium, where (55) can be used and ρ_B is isotropic, $\vec{\mathrm{P}}^{(1)}$ is parallel to $\vec{\mathrm{E}}_k$; i.e.,

$$P_i^{(1)} = \delta_{ik}P_k^{(1)}\,, \tag{58}$$

where μ_k has been used as one of three Cartesian components of $\vec{\mu}$.

The introduction of projection operators allows us to use the method of Zwanzig[1] and write

$$DG(\omega)D = D(\omega - L + i\epsilon)^{-1}D$$

$$= [\,\omega - DLD - \Sigma(\omega)\,]^{-1}\,, \tag{59}$$

where, with

$$C = 1 - D \tag{60}$$

as the projection operator complementing D,

$$\Sigma(\omega) = DLC(\omega - CLC + i\epsilon)^{-1}\,CLD\,. \tag{61}$$

The operator D has the property of projecting out a part of the system's dipole subspace. Thus, DLD is a matrix of dipole resonance frequencies of the system. The remaining term $\Sigma(\omega)$ in (59) is a complex "mass operator," also known as the "memory function" which has been studied extensively in the linear-response theory.[1,16,17] Its anti-Hermitian part is a matrix of relaxation rates for the system, and its Hermitian part is a matrix of pressure shifts.

In the nonlinear case we can extend this treatment to the harmonics-number representation. The projection operators commute with the raising and lowering operators, since they operate on different degrees of freedom. Therefore we can write by applying the projection-operator method to (40), and in analogy with (57),

$$P_i(\vec{\mathrm{n}}\cdot\vec{\omega}) = -\tfrac{1}{2}\hbar^{-1}(N/V)$$

$$\times\sum_k\sum_\pm\{\langle\langle\mu_i;\vec{\mathrm{n}}\,|D\mathcal{G}D\mathcal{E}_k^{\pm}|\,\mu_k\rho_e;\vec{0}\rangle\rangle$$

$$-\langle\langle\mu_i;\vec{\mathrm{n}}\,|\,D'\,\mathcal{G}D'\mathcal{E}_k^{\pm}\,|\,\rho_e\mu_k;\vec{0}\rangle\rangle\}\,. \quad (62)$$

Here again, using Zwanzig's method we can write

$$D\mathcal{G}D = [\,\omega - DL'D - DL'C(\omega - CL'C + i\epsilon)^{-1}CL'D\,]^{-1}\,, \quad (63)$$

where we have replaced the L of the linear-response approximation by

$$L' = L + W\,. \quad (64)$$

VI. SHORT-MEMORY APPROXIMATION

In Eq. (63) the mass operator is composed of entangled collisional and radiational interactions, owing to the substitution of the modified Liouvillian L'. We now seek an approximation by which the two chains of processes can be disentangled.

Consider the Dyson equation

$$D\mathcal{G}D = DGD + DGW\mathcal{G}D\,. \quad (65)$$

The disentanglement can be achieved if we replace W by its projection onto the system subspace DWD, i.e.,

$$D\mathcal{G}D \simeq DGD + DGDWD\mathcal{G}D\,. \quad (66)$$

The vectors on which D projects describe an elementary excitation of a single molecule where the rest of the sample is in complete chaos (ρ_e). The modification introduced by (66) therefore means that at the onset of each interaction with a photon, the rest of the sample is supposed to be in thermal equilibrium, with no memory of its past history, except for the elementary excitation of the system. In the language of Feynman diagrams[3,4] (see examples in Fig. 1) this means that no interaction between the system and the bath extends across an intermediate photon line. Such a condition holds only if the bath has a short memory of its interaction with the system, so that there is only a negligible chance that it may be in nonequilibrium at the time of interaction with the radiation. This condition is compatible with the impact approximation,[14,18] commonly used with dilute systems, in which the duration of each perturbation of the bath is short. Therefore, approximation (66) is valid whenever the impact approximation is valid [although the opposite is not necessarily true, as can be seen from the right-hand side of example (a) in Fig. 1].

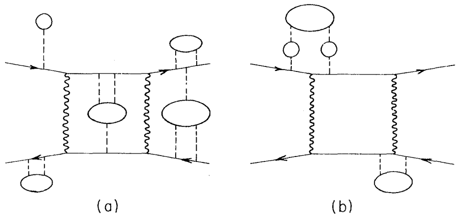

FIG. 1. Examples of intermediate photon Feynman diagrams that are (a) allowed or (b) forbidden in the short-memory approximation. Open lines—system propagators, closed loops—bath propagators, wavy lines—photon lines, and broken lines—collisional interactions. The opposing arrows denote the lower and upper states of an optical line, in accordance with the notations of Refs. 3 and 4.

By simple algebraic manipulation it can be shown that

$$D\,\mathcal{G}WG = DGD[1 + LC(\omega - CLC + i\epsilon)^{-1}C\,]W\mathcal{G}\,. \quad (67)$$

The second part of (67) involves the product CW, or CU, which means that the interaction U occurs while the sample is not in the state of elementary excitation described by D. Neglect of CW as well as of WC (which allows us to replace W by DWD), leads us to the short-memory approximation (66). In the resulting expression

$$D\mathcal{G}D = [\omega - DLD - DWD - \Sigma(\omega)]^{-1}\,, \quad (68)$$

the collisional and radiational effects in the denominator are disentangled.

We have avoided so far the mention of space degeneracy and the accompanying symmetry considerations. These will be postponed to Sec. VII. Here we shall state the two additional approximations needed in order to reach the practical level we have set forth to obtain.

First is the impact approximation, already mentioned above. In this approximation the collisional interactions are assumed to have very short correlation times. (These finite correlation times lead to a suppression of the tails of collision-broadened lines.) With this assumption $\Sigma(\omega)$ is made a constant matrix, independent of ω; its Hermitian part is the matrix of pressure shifts and its anti-Hermitian part is the matrix of relaxation and cross-relaxation rates of the set of modes included in our projected subspace.[19]

The second approximation, which is also particularly suitable to dilute gases, is to assume that the absorption spectrum is confined to sharp resonance lines. In this approximation we neglect $G(\omega)$ whenever ω is far (in terms of the linewidth) from a resonance frequency of the absorbing system.

VII. SYMMETRY CONSIDERATIONS

In isotropic media, the electric dipole forms a basis for a particular irreducible representation of the inversion-rotation group, under which L, and therefore G, are invariant. Let us denote a component of each basis by the three numbers Π, K, Q, where $\Pi=\pm 1$ denotes the parity, $2K+1$ $(K=0,\ 1,\ 2\ldots)$ denotes the multiplicity, and the $2K+1$ values of $Q=-K,\ \ldots\ K$ denote the members of the multiplet.[20] Electric dipoles belong to the irreducible representation $\Pi=-1$, $K=1$.

In the linear-response approximation, the expression of the u_α's in terms of the multiplets Π, K, Q suffices for a reduction of the Green's function by inversion-rotation symmetry. If G is invariant under inversion and rotations in the complete sample's space, then by decoupling the system from the bath by (55) and averaging over the isotropic thermal bath it is also invariant in the system's subspace alone. Each multipole has its own reduced Green's function $G^{(\pi,k)}$.

This is not true in the nonlinear case, when W is considered. The product of two M's in W is not invariant, and can transfer the system from one multipolar excitation to another, according to the rules of vector coupling. If we want to retain the disentanglement achieved by the weak coupling approximation, we ought to modify it by introducing a less restrictive form of projection operators in one of the two following methods.

One method is to insert before and after the W in (66) the bath projection operator D_B instead of the complete D. In this way we only retain the bath averaging of each G separately, and leave intact the multipole-changing character of W. Thus,

$$\begin{aligned} D\mathcal{G}D &\simeq DGD+DGD_BWD_B\mathcal{G}D \\ &=DGU\langle G\rangle U\mathcal{G}D\ , \end{aligned} \tag{69}$$

where the angular brackets denote a bath average. Each G in the ensuing series is now confined to a multipole different from that of its neighbors, with the first and last G in each term lying in the electric dipole subspace. In the intermediate G's we have to sum over all values of K allowed by dipole selection rules (Π being fixed for each G as alternatingly positive and negative by the odd parity of M).

The alternative method is to extend the definition of the projection operator D to include all u_α's degenerate with the original u_α of dipole character, belonging to the same pair a, b of energy levels but to all possible multipoles. Thus, instead of having to deal with the single term[20] $|\,ab^+;\ \Pi KQ\rangle\rangle$, with $\Pi=-1$, $K=+1$, we shall have to consider all possible $|\,am_a,\ (bm_b)^+\rangle\rangle$, with various magnetic quantum numbers m_a and m_b in the levels of a and b, respectively. In either way we must give up the simplicity introduced by spherical symmetry in the linear-response theory.

The related problem of space degeneracy in saturated magnetic dipole spectra (i.e., spin resonance) has been solved in more detail by Freed.[21]

VIII. SATURATION OF TWO-LEVEL SYSTEM

Consider a pair of energy levels a, b, where the resonance frequency

$$\omega_{ab}=(E_a-E_b)/\hbar>0 \tag{70}$$

corresponds to an isolated transition allowed by electric dipole selection rules. Suppose the transitions $a\rightarrow a$ and $b\rightarrow b$ are forbidden by the same selection rules. Forgetting, for the time being, space degeneracy, we have altogether four vectors to the absorbing system's Liouville space. Two of them $|\,ab^+\rangle\rangle$ and $|\,ba^+\rangle\rangle$ are dipole allowed, and the other two $|\,aa^+\rangle\rangle$ and $|\,bb^+\rangle\rangle$ are dipole forbidden. If a and b are also parity eigenstates, then the first two vectors must have odd parity and the second two even. Therefore the G's between the W's in the Dyson series all lie in the odd subspace, whereas the G's within the W's are in the even subspace. In the first case, where G is confined to the two-dimensional space of $|\,ab^+\rangle\rangle$ and $|\,ba^+\rangle\rangle$, its bath average can be written as[19]

$$\langle G\rangle=[\omega I-\Phi+i\Gamma_1]^{-1}\ , \tag{71}$$

where I is the unit matrix,

$$\Phi=\begin{pmatrix}\omega_{ab}+\delta & 0\\ 0 & -\omega_{ab}-\delta\end{pmatrix} \tag{72}$$

(where to ω_{ab} is added the pressure shift δ) and where

$$\Gamma_1=\begin{pmatrix}\gamma_{ab} & -\zeta\\ -\zeta & \gamma_{ab}\end{pmatrix}\ , \tag{73}$$

γ_{ab} being the linewidth and ζ the cross-relaxation rate for mixing a with b. If the lines are sufficiently sharp, so that $\gamma_{ab}\ll\omega_{ab}$, we can consider[19] only the first diagonal element in Φ and Γ_1, when $\omega\simeq\omega_{ab}$, and the second one when $\omega\simeq-\omega_{ab}$, neglecting the off-diagonal element ζ. The only elements we thus consider are

$$\begin{aligned} &\langle\langle\,ab^+\,|\,\langle G(\omega)\rangle\,|\,ab^+\rangle\rangle=(\omega-\omega_{ab}-\delta+i\gamma_{ab})^{-1}\equiv G_{ab}(\omega)\ , \\ &\langle\langle\,ba^+\,|\,\langle G(-\omega)\rangle\,|\,ba^+\rangle\rangle=-G^*_{ab}(\omega)\,. \end{aligned} \tag{74}$$

In the second case, where G is confined to the space $|\,aa^+\rangle\rangle$, $|\,bb^+\rangle\rangle$, we have

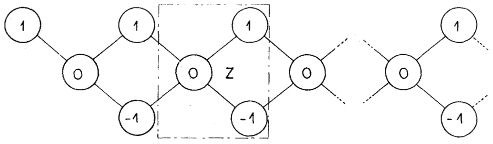

FIG. 2. Typical diagram for the saturation of a resonance line by a monochromatic field. Circles represent Green's functions $G(n\omega)$, the encircled numbers being the harmonics numbers n. Connecting line represent an interaction $U=-\frac{1}{2}ME$. The diagram is composed of a succession of links, such as the one enclosed in the rectangle Z.

$$\langle G\rangle=(\omega I+i\Gamma_0)^{-1}\,, \tag{75}$$

where

$$\Gamma_0=\begin{pmatrix}\gamma_a & -\sigma\\ -\sigma & \gamma_b\end{pmatrix}\,. \tag{76}$$

Here γ_a and γ_b are, respectively, the inverse lifetimes of levels a and b, and σ is the rate of transitions from a to b. In this case, unlike that of (73), we have to consider all four elements whenever $\omega\simeq 0$, since both γ_a and γ_b belong to the same (zero) resonance frequency.

The sample is irradiated with a monochromatic beam polarized, for example, in the z direction. Vectors in the even-parity subspace are transformed by the operator M into vectors in the odd-parity subspace. Thus, we have

$$\begin{aligned}\hbar M\,|\,ab^{+}\rangle\rangle&=\mu_{ba}(\,|\,bb^{+}\rangle\rangle-|\,aa^{+}\rangle\rangle)\,,\\ \hbar M\,|\,ba^{+}\rangle\rangle&=-\mu_{ab}(\,|\,bb^{+}\rangle\rangle-|\,aa^{+}\rangle\rangle)\,,\\ \hbar M\,|\,aa^{+}\rangle\rangle&=-\hbar M\,|\,bb^{+}\rangle\rangle=\mu_{ba}\,|\,ba^{+}\rangle\rangle-\mu_{ab}\,|\,ab^{+}\rangle\rangle\,.\end{aligned} \tag{77}$$

In the calculation of $\vec{\mathrm{p}}(\omega)$ we may retain, by our assumption of sharp lines, only the $\vec{\mathrm{n}}\cdot\vec{\omega}=\pm\omega$ terms at the odd-parity stages, and $\vec{\mathrm{n}}\cdot\vec{\omega}=0$ at the even-parity stages. Therefore, terms in the Dyson series can be represented by the diagram shown in Fig. 2. As we calculate the polarization at the fundamental frequency ω, all diagrams should end on the left with $n=+1$. The Dyson series can then be written as

$$\mathcal{G}(\omega)=\sum_{j=0}^{\infty}G_{ab}(\omega)Z^{j}\,, \tag{78}$$

where

$$Z=\tfrac{1}{4}\textstyle\sum_{\pm}M\langle G(0)\rangle M\langle G(\pm\omega)\rangle\,|\,E_k\,|^{2} \tag{79}$$

represents a link in the chain. Summing the geometric progression (78), we have

$$\begin{aligned}\mathcal{G}(\omega)&=G_{ab}(\omega)(1-Z)^{-1}\\ &=[G_{ab}{}^{-1}(\omega)-ZG_{ab}{}^{-1}(\omega)]^{-1}\,.\end{aligned} \tag{80}$$

Consider now the effect of Z on $M\,|\,\rho_e\rangle\rangle$,

$$\begin{aligned}ZM\,|\,\rho_e\rangle\rangle&=Z(\rho_b-\rho_a)\,\hbar^{-1}(\mu_{ab}\,|\,ab^{+}\rangle\rangle-\mu_{ba}\,|\,ba^{+}\rangle\rangle)\\ &=\tfrac{1}{4}\hbar^{-2}\,|\,E_k\,|^{2}(\rho_b-\rho_a)\,|\,\mu_{ab}\,|^{2}[G_{ab}(\omega)-G^{*}_{ab}(\omega)]M\langle G(0)\rangle(\,|\,bb^{+}\rangle\rangle-|\,aa^{+}\rangle\rangle),\end{aligned} \tag{81}$$

where (74) has been used for $G(\pm\omega)$. Using (75) and (76) for $G(0)$, we obtain

$$\begin{aligned}ZM\,|\,\rho_e\rangle\rangle=\hbar^{-2}\,|\,E_k\,|^{2}\,|\,\mu_{ab}\,|^{2}(\gamma_a\gamma_b-\sigma^{2})^{-1}\\ \times(\tfrac{1}{2}\gamma_a+\tfrac{1}{2}\gamma_b-\sigma)[\mathrm{Im}\,G_{ab}(\omega)]M\,|\,\rho_e\rangle\rangle\,,\end{aligned} \tag{82}$$

i.e., Z is diagonal in $M\,|\,\rho_e\rangle\rangle$. Now, we have

$$\mathrm{Im}\,G_{ab}(\omega)=-\gamma_{ab}\,|\,G_{ab}(\omega)\,|^{2}\,. \tag{83}$$

Therefore, using (81)–(83), the sum of the two contributions to the polarization [see Eq. (62)] at $\vec{\mathrm{n}}\cdot\vec{\omega}=\omega$ is given by

$$\begin{aligned}\mathcal{G}(\omega)&=[G_{ab}{}^{-1}(\omega)+\eta\hbar^{-2}\,|\,\mu_{ab}\,|^{2}\,|\,E_k\,|^{2}G^{*}_{ab}(\omega)]^{-1}\\ &=\frac{\omega-\omega_{ab}-\delta+i\gamma_{ab}}{(\omega-\omega_{ab}-\delta)^{2}+\gamma_{ab}{}^{2}+\eta\hbar^{-2}\,|\,\mu_{ab}\,|^{2}\,|E_k\,|^{2}}\,,\end{aligned} \tag{84}$$

where

$$\eta=(\gamma_a\gamma_b-\sigma^{2})^{-1}\gamma_{ab}(\tfrac{1}{2}\gamma_a+\tfrac{1}{2}\gamma_b-\sigma)\,. \tag{85}$$

This dimensionless coefficient modifies the result of Karplus and Schwinger[7] (equivalent to $\eta=1$), which is obtained under the assumption that $\gamma_{ab}=\gamma_a=\gamma_b$ and $\sigma=0$. In actual collision-broadening problems γ_{ab} may be quite different from γ_a or γ_b, and in low-frequency (microwave) spectra, the effect of σ is not negligible.

The introduction of space degeneracy complicates the problem. By choosing $\vec{\mu}$ to be along the z axis, and assuming we can average each G alone over the isotropic bath, we restrict ourselves to Liouville-space vectors with $Q=0$ (i.e., transitions with $\Delta m=0$). Consider the transition $j_a=1\rightarrow j_b=0$, where j_a and j_b are, respectively, the angular momenta of levels a and b. Here $|\,ab^{+}\rangle\rangle$ and $|\,ba^{+}\rangle\rangle$ are confined to the dipole subspace, and $|\,bb^{+}\rangle\rangle$ to the monopole subspace ($K=0$), but $|\,aa^{+}\rangle\rangle$ is a mixture of a monopole and a quadrupole ($K=0$ and 2). Therefore Z and, hence, η consist of two terms, e.g.,

$$\eta=c^{(0)}\eta^{(0)}+c^{(2)}\eta^{(2)}\,, \tag{86}$$

one for the monopole and the other for the quadrupole contribution of $|\,aa^{+}\rangle\rangle$. The coefficients $c^{(i)}$ ($i=0$ or 2) are the squares of the projections of

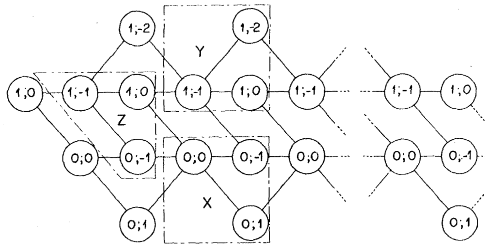

FIG. 3. Typical diagram for the linear response at a resonance line to a monochromatic field E_1 at the presence of a saturating field E_2. Circles represent Green's functions $G(n_1\omega_1+n_2\omega_2)$, the enclosed number pairs being n_1; n_2. Connecting lines represent an interaction $U=-\frac{1}{2}ME$. The diagram is composed of various combinations of a succession of X links, followed by a Z link and then by a succession of Y links. The various types of links are shown by rectangles.

$|\, aa^+\rangle\rangle$ on the corresponding multipole subspaces, normalized so that their sum is unity. Each $\eta^{(i)}$ has its own γ_a, γ_b, and σ. A similar result may be obtained also for other j values if we neglect the projections of $|\, ab^+\rangle\rangle$ and $|\, ba^+\rangle\rangle$ on multipole subspaces other than the dipole.

IX. TWO-FIELD PROBLEM

Consider now the response of a dilute sample to a weak monochromatic field E_1 in the presence of a strong saturating field E_2, where the corresponding frequencies ω_1 and ω_2 are near a resonance frequency, i.e.,

$$\omega_1 \simeq \omega_2 \simeq \omega_{ab} \,. \tag{87}$$

In this case, assuming sharp resonance, we need to consider only the following matrix elements:

$$\begin{aligned} &G_{ab}(n_1\omega_1+n_2\omega_2)\equiv G_{ab}(n_1;\, n_2)\,,\\ &G_{ba}(-n_1\omega_1-n_2\omega_2)\equiv G_{ba}(-n_1;\, -n_2)\,, \end{aligned} \tag{88}$$

with

$$n_1=0\pm 1,\ \pm 2,\ \ldots\,, \qquad n_2=1-n_1\,, \tag{89}$$

and the matrix elements of

$$\langle G(n\omega_1-n\omega_2)\rangle \equiv G(n;\, -n) \qquad (n=0,\ \pm 1,\ \pm 2\ldots)\,, \tag{90}$$

in the 2×2 subspace of $|\, aa^+\rangle\rangle$ and $|\, bb^+\rangle\rangle$ [for the same reasons as in Eq. (75)]. Here all the diagrams should end up with $G_{ba}(\omega_1)$ on the left since we are interested in the polarization at ω_1.

A typical diagram is shown in Fig. 3, where each pair of numbers denotes the two harmonics numbers n_1 and n_2. Here we have limited the analysis to responses linear in E_1, under the assumption that E_1 is weak, but have retained all powers of E_2.

In following any possible trajectory in the diagram, going from right to left, we can therefore vary n_2 as many times as desired, restricted only by (89) or (90). But n_1 can be changed from 0 to 1 only once along each trajectory. Three types of links can therefore be found in these diagrams:

$$\begin{aligned} X&=\tfrac{1}{4}\hbar^{-2}G_-(0;\, 0)[G_{ab}(0;1)+G_{ab}(0;\, -1)]\,|\,\mu_{ab}E_2\,|^2\,,\\ Y&=\tfrac{1}{4}\hbar^{-2}G_-(1;\, -1)[G_{ab}(1;0)+G_{ba}(1;\, -2)]\,|\,\mu_{ab}E_2\,|^2\,,\\ Z&=\tfrac{1}{4}\hbar^{-2}G_-(1;\, -1)[G_{ba}(0;\, -1)+G_{ab}(1;\, 0)]\,|\,\mu_{ab}E_2\,|^2\,, \end{aligned} \tag{91}$$

where

$$\begin{aligned} G_-=\langle\langle aa^+\,|\,\langle G\rangle\,|\,aa^+\rangle\rangle+\langle\langle bb^+\,|\,\langle G\rangle\,|\,bb^+\rangle\rangle\\ -\langle\langle aa^+\,|\,\langle G\rangle\,|\,bb^+\rangle\rangle-\langle\langle bb^+\,|\,\langle G\rangle\,|\,aa^+\rangle\rangle\,. \end{aligned} \tag{92}$$

Here X describes a two-photon step along the chain of events before the single jump in n_1, Y describes such a step after the jump, and Z is a connecting link between the two chains. In reaching the $G_{ab}(1;\, 0)$ on the left we can either follow the chain of X's or jump to the Y chain via a Z step. Therefore, the jth order diagram will give

$$\mathcal{G}^{(j)}(\omega_1)=G_{ab}(1;0)\left(X^j+\sum_{k=0}^{j-1}Y^kZX^{j-k-1}\right). \tag{93}$$

As in the case of saturation discussed in Sec. VIII, here also the X, Y, and Z are diagonal in $M\,|\,\rho_e\rangle\rangle$, and can be replaced by scalar numbers.

Performing the summation over k in (93) we obtain

$$\begin{aligned} \mathcal{G}^{(j)}(\omega_1)&=G_{ab}(1;0)X^j\left(1+\frac{Z}{X}\sum_{k=0}^{j-1}\frac{Y}{X}\right)\\ &=G_{ab}(1;\, 0)[X^j+Z(X-Y)^{-1}(X^j-Y^j)]\,, \end{aligned} \tag{94}$$

and, summing over all orders,

$$\begin{aligned} \mathcal{G}(\omega_1)&=\sum_{j=0}^{\infty}\mathcal{G}^{(j)}(\omega_1)\\ &=G_{ab}(1;0)\left[\frac{1}{1-X}+\frac{Z}{X-Y}\right.\\ &\qquad\left.\times\left(\frac{1}{1-X}-\frac{1}{1-Y}\right)\right]\,. \end{aligned} \tag{95}$$

The ratio of $\mathcal{G}(\omega_1)$ to $G_{ab}(1;0)$ is also the ratio of the susceptibility of the sample at frequency ω_1 in the presence of the saturating field E_2 to that in its absence. This ratio

$$f(\omega_1;\, \omega_2)=\frac{\mathcal{G}(\omega_1)}{G_{ab}(1;\, 0)}=\frac{(1+Z-Y)}{(1-X)(1-Y)} \tag{96}$$

depends on the difference between ω_1 and ω_2. As ω_1 approaches ω_2, we have $X=Y=Z$, and the ratio reduces to

$$f(\omega_2;\, \omega_2)=(1-X)^{-2}\,. \tag{97}$$

This is the *square* of the factor obtained in the case of saturation as the correction to the linear-response polarization. But when $\omega_1 = \omega_2$, we cannot distinguish between the two fields, and the polarization should be equal to that of the Sec. VIII. We therefore expect a "discontinuity" in the polarization as we let ω_1 of the weak field pass through ω_2 of the strong field. This discontinuity is formally accounted for by certain δ functions in $\delta\rho(\omega)$ which contribute only when $\omega_1 = \omega_2$. In reality, "monochromatic" beams have a finite bandwidth, and therefore this discontinuity will occur smoothly over a finite range of the frequency difference. This phenomenon results from the indistinguishability of ω_1 from ω_2 photons when $|\omega_1 - \omega_2|$ lies within the bandwidth. It is thus reminiscent of the Lamb dip,[22] which is usually associated with the indistinguishability of forward- and backward-moving photons as seen by a molecule at rest.

X. CONCLUSIONS

The method developed and illustrated above is generally applicable to problems involving the nonlinear response of a system of several levels to several monochromatic beams, such as is encountered in the phenomena listed in the Introduction. In dealing with complicated situations, although it may become necessary to replace numerical coefficients of the kind in (91) by matrices of small dimensions, series summations of the type occuring in (95) can still be performed.

Our analysis traces back the origin of the approximations (such as short memory) leading to the ordinary phenomenological treatments of the collision effects, and can therefore serve as a basis for extension to cases where these approximations are not valid. Its major point, however, is the recognition that diagrammatic methods for series summation, introduced by a formalism of "second quantization," are also applicable to classical fields.

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[†] Visiting professor at the Weizmann Institute of Science, Rehovot, Israel, 1969.

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