

## Superradiant Level Shift and Its Possible Detection in a Transient Optical Experiment

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The superradiant level shift of a system of  $N$  two-level molecules, interacting with the radiation field, is calculated for pencil-like geometry. Introducing the self-energy  $\Sigma^{(N)}(E)$  of the molecular systems due to its radiative interaction, we first discuss the trivial ( $N=1$ ) and familiar ( $N=2$ ) cases in more detail. The analytic properties of the self-energy  $\Sigma^{(N)}(E)$  are used to derive dispersion relations for its real and imaginary parts  $\Delta^{(N)}(E)$ ,  $\Gamma^{(N)}(E)$ . We then generalize to the case of  $N \gg 1$ , employing a self-consistency argument advanced by Arecchi and Courtens. The modified Dicke expression for the cooperative spontaneous decay rate is then used in the dispersion relation for the shift  $\Delta^{(N)}$  and a value of  $\sim 6$  MHz calculated corresponding to typical molecular-gas parameters. The physical measurability of the shift is discussed and a Brewer-Shoemaker experiment in a molecular gas is proposed for the observation of the shift.

### I. INTRODUCTION

A considerable number of papers<sup>1-15</sup> have appeared on various aspects of superradiance since the introduction of the concept by Dicke.<sup>1</sup> Cooperative effects between different atoms due to their common interaction with the radiation field are of considerable interest for the correct description of highly excited states of matter and their return to equilibrium. The correlations implicit in the common interaction with the radiation field can be conveniently described quantum mechanically by treating the assembly of atoms as a *single*-quantum system.<sup>1</sup> Alternatively, some of the results on radiation damping and coherence can be treated in semiclassical fashion by relating the time evolution of the superradiant states  $|rm\rangle$  to Bloch-like equations.<sup>15</sup>

Experimental consequences of the many-body correlations implicit in superradiance are the optical analogs of the earlier magnetic coherence phenomena, due to coherent spin motions such as NMR, spin echoes, transient nutation, free-induction decay, and others. Although all of these have been observed in the last ten years<sup>16-20</sup> and a very dramatic consequence of the coherent resonant atom-field interaction was discovered in the phenomenon of self-induced transparency,<sup>21,22</sup> most of the experimental demonstrations of cooperative effects have been hampered by the difficulty of preparing suitably well-defined optical pulses and matching their frequencies to absorption frequencies in the system under study. The discreteness of available laser frequencies therefore forces the experimentalist to a search for accidental spectral coincidence of pulse source (laser) and absorber unless these are identical, as in the early photon-echo experiments in ruby. Needless to say, the development of continuously tunable lasers (e.g., dye lasers) should eliminate this undesirable limi-

tation on experiments. The technique recently introduced by Brewer and Shoemaker for the study of molecular coherence<sup>23</sup> circumvents the difficulties implicit in optical pulse preparation. The central idea is to use an external field (electric or magnetic) to shift the states under study in and out of resonance with a continuously applied laser field. As the control of the external field is easily attainable by electronic circuitry and not via the complicated dynamics of lasing action in a cavity, the preparation of  $\frac{1}{2}\pi$ ,  $\pi$ ,  $n\pi$  pulses is no longer problematic.

It is the ease of the control of the temporal evolution of the molecular system in the presence (absence) of a resonant strong radiation field which leads to the proposed experimental observation of the effect discussed in this paper.

This effect is the appearance of a shift of the emitted radiation as a consequence of the *different* virtual radiative effects on the energy levels of the  $N$  coupled molecules.<sup>24</sup> In its origin, it is analogous to the Lamb shift, which describes the difference of the radiative corrections of  $s$  or  $p$  electrons in the Coulomb field of the nucleus compared to free electrons. The role of the Coulomb field of the nucleus is played in the superradiant case by the effect of the field of the  $N-1$  excited (unexcited) molecules on the  $N$ th one. Although radiative shifts of single-particle states are, in general, already included in the physical (renormalized) energy of the particular state under consideration, in the case of superradiance the shift becomes observable as a frequency shift of the emitted photons from the single-molecule transition frequency. Equivalently, one can say that the assumption of equal spacing between the  $N$ -molecule eigenstates is incorrect, as radiative corrections shift different eigenstates differently and consequently the emitted photons at different stages of the transition of the entire  $N$ -molecule system to the ground

state have different frequencies.

These effects are most conveniently studied by the use of the self-energy concept and renormalization, which systematically includes the effect of interaction on the eigenvalues of a given system. For graphic illustration, Feynman diagrams and the standard ways of summing infinite subsets of important diagrams by use of the Dyson equation are occasionally employed.

An outline of the results presented in this paper is now given. Section II considers the trivial case of  $N=1$  to define the notation and terminology. The real part  $\Delta^{(1)}(E)$  of the (lowest-order) self-energy  $\Sigma^{(1)}$  is not experimentally accessible, as the interaction with the spontaneous radiation field is always present, and consequently only the renormalized eigenvalue of the excited state is measured in an experiment as the frequency of the emitted photon.<sup>25(b)</sup> The imaginary part  $\Gamma^{(1)}$ , however, can be measured and accounts for the finite lifetime of the excited state ( $\tau = \pi/\Gamma^{(1)}$ ). This is no longer so for  $N=2$ , the next case considered, as the presence of the second molecule provides an additional field (the dipole field of the transition dipole plays the role of the nuclear Coulomb potential in the Lamb shift), which renormalizes the superradiant system of two molecules—one excited, the other unexcited—considered earlier by a number of authors<sup>3,13,26</sup> in a qualitatively new and different way. Apart from the usual single-particle self-energy terms  $\Sigma^{(1)}$  inserted in the excited-state propagator, there are energy-transfer terms (see Fig. 2), which lead to a distance-dependent self-energy containing both a physically measurable shift  $\Delta^{(2)}(E)$  as well as a width  $\Gamma^{(2)}(E)$ . In fact, the discussion of just such a system of two spins provided the point of departure of Dicke's classic paper. The treatment given there was confined, however, to the effect of cooperative spontaneous decay, i. e., consideration of the radiation rate and angular photon correlations of such systems. It is, of course, well known that a decay rate calculated by the Fermi golden rule is exactly equivalent to the imaginary part of the appropriate self-energy diagram (the energy-conserving  $\delta$  function converts the intermediate-state sum directly into a density of states, while the matrix element is just the interaction vertex, responsible for the coupling). To lowest order then, Dicke's result for the spontaneous decay rate leads to the much heralded result  $\gamma_N = \frac{1}{4}N^2\gamma_0$ .

It is of interest to point out the consequences of considering the next-higher-order corrections, summed selectively to infinite order, on the spectrum of the superradiant emission. This shift of the eigenfrequencies was not considered by Dicke, but has been discussed by a variety of authors,<sup>25-28</sup> both for small  $N(<10)$  and large  $N(>>1)$ . The ap-

proach based on the analytic properties of the self-energy  $\Sigma^{(N)}(E)$ , which follows from the retarded nature (causality) of the interaction between the molecules for  $N=2$ , is illustrated. The use of the dispersion relation (Hilbert transform) between the real and imaginary parts of  $\Sigma^{(2)}(E)$  leads directly to the familiar result by employing a suitable contour integration.

In Sec. III the case  $N \gg 1$  in a needlelike geometry characterized by a small Fresnel number is considered. The self-consistent argument, recently proposed by Arecchi and Courtens<sup>13</sup> to determine the maximal number  $N_c$  of molecules radiating cooperatively with a spectral width  $\gamma_c$ , is used. These parameters, called the cooperation number  $N_c$  and cooperation time  $\tau_c = \pi/\gamma_c$  (width of the superradiant pulse) have been also found by other workers<sup>11</sup> to be crucial for the characterization of the superradiant pulse and the appearance of self-induced transparency.

This argument is reproduced and is furthered by equating the imaginary part of the  $N$ -molecule self-energy  $\Sigma^{(N)}(E)$  with  $\gamma_c$  so derived. The  $N$ -molecule superradiant shift  $\Delta^{(N)}(E)$  is then calculated as the Hilbert transform of the width function  $\gamma_c(E')$ , i. e., as a principal-value integral over all frequencies. Physical considerations about the limiting frequencies of the particular problem studied lead to the introduction of an infrared cutoff  $\omega_{\min} = 2\pi c/L$  and a high-frequency cutoff  $\omega_{\max} = 2\pi c/D$  ( $L$  is the sample length;  $D$  is the molecular diameter).

Section IV considers the possible experimental observation of the superradiant level shift in a transient optical experiment of the type recently reported by Brewer and Shoemaker.<sup>23</sup> It is argued that the coherent preparation of the system (a molecular gas) pumped by a cw laser beam can be considered to be close to the  $|rm=0\rangle$  state and that the Stark shifting of the particular velocity group excited resonantly via the Doppler shift simulates the requirement of spontaneous cooperative emission necessary for superradiance as the laser photons are sufficiently off-resonant for the originally excited velocity group. It is noted that some care has to be taken in Stark shifting in times short compared to the inverse calculated shift in order to prevent a smearing out of the frequency shift. The shifted superradiant emission is observed by looking for a beat pattern with the laser in a square-law detector. Section V contains a summary of the results and the conclusions concerning the general applicability and significance of our approach.

## II. RADIATIVE CORRECTIONS FOR $N=1$ AND $N=2$ ; SIMPLEST SUPERRADIANT SYSTEM REVISITED

This section begins by going over familiar ground [for an excellent review, see Ref. 29(b)] and dis-

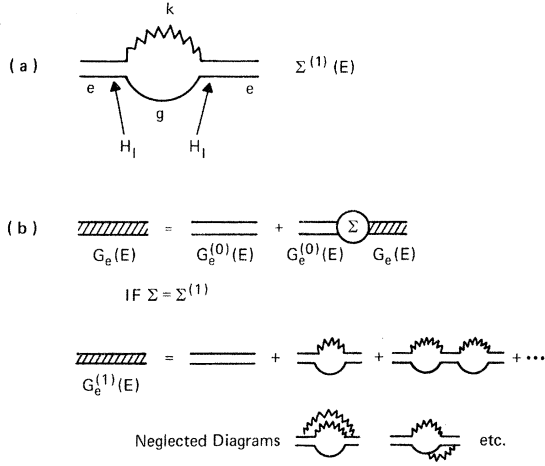


FIG. 1. Lowest-order self-energy  $\Sigma^{(1)}(E)$  for  $N=1$  and selective summation by Dyson equation.

cusses a single ( $N=1$ ) two-level system interacting with the radiation field in the electric-dipole approximation described by the Hamiltonian  $H = H_0 + H_I$ ,

$$H_0 = \frac{1}{2}\omega_0 \sigma_z + \sum_k \omega_k a_k^\dagger a_k, \quad (1)$$

$$H_I = \sum_k (\vec{\epsilon}_k \cdot \vec{p})(a_k \sigma_+ + \sigma_- a_k^\dagger),$$

where  $\omega_0$  is the molecular level spacing  $E_e^{(0)} - E_g^{(0)} = \omega_0$ ;  $\sigma_+$ ,  $\sigma_-$ ,  $\sigma_z$  are components of the  $2 \times 2$  Pauli spin matrices, which represent the density matrix of the two-level system; and  $a_k^\dagger$ ,  $a_k$  are the photon creation and annihilation operators. The states of the system are  $|e\rangle$ ,  $|g\rangle$  for the excited- and ground-state (two-level) molecule wave function and  $|n_k\rangle$  for the number eigenstates for the  $k$ th mode of the radiation field. They obey the relations

$$\begin{aligned} \sigma_+ |g\rangle &= |e\rangle, & \sigma_+ |e\rangle &= 0; \\ \sigma_- |e\rangle &= |g\rangle, & \sigma_- |g\rangle &= 0; \\ \sigma_z |g\rangle &= -|g\rangle, & \sigma_z |e\rangle &= |e\rangle; \\ a_k^\dagger |n_k\rangle &= (n_k + 1)^{1/2} |n_k + 1\rangle, \\ a_k |n_k\rangle &= (n_k)^{1/2} |n_k - 1\rangle; \end{aligned} \quad (2a)$$

and the commutation relations

$$\begin{aligned} [\sigma_\pm, \sigma_z] &= \pm 2\sigma_\mp, \\ [a_k, a_{k'}^\dagger] &= \delta_{kk'}. \end{aligned} \quad (2b)$$

Natural units  $\hbar = c = 1$  are used.

To study spontaneous emission, this paper is interested in the time evolution of the state  $|e\rangle|0\rangle$  under the action of  $H_I$  with initial condition

$$\psi(t=0) = |e\rangle|0\rangle. \quad (3)$$

The time-evolution operator  $U(t)$ , which is defined as

$$\psi(t) = U(t)\psi(0), \quad (4)$$

can be represented in the form

$$U(t) = (1/2\pi i) \int_{-\infty}^{\infty} G_e(E) e^{-iEt} dE, \quad (5)$$

and  $G_e(E)$  is the appropriate Green's function (propagator) of the excited state,

$$G_e(E) = P_e(E - H + i\epsilon)^{-1} P_e, \quad (6)$$

$$P_e = 0 |e\rangle\langle e| \langle 0|. \quad (6)$$

Using the standard Feynman-Dyson approach to perturbation theory,<sup>30</sup> Eq. (6) can be reexpressed in terms of an integral equation for  $G_e(E)$ , i. e.,

$$G_e(E) = G_e^{(0)}(E) + G_e^{(0)}(E) \Sigma(E) G_e(E), \quad (6a)$$

where  $\Sigma(E)$  is the sum of all irreducible self-energy diagrams and  $G_e^{(0)} = P_e(E - H_0 + i\epsilon)^{-1} P_e$ .

In Fig. 1(a) the lowest-order self-energy  $\Sigma^{(1)}(E)$  is exhibited, and the Dyson equation automatically sums its contribution to infinite order [Fig. 1(b)].

One therefore finds for an approximate solution of Eq. (6), however summed to infinite order ( $E_e^{(0)} = \frac{1}{2}\omega_0$ ),

$$G_e^{(1)}(E) = [E - E_e^{(0)} - \Sigma^{(1)}(E)]^{-1}, \quad (6b)$$

and substituting in Eq. (4) and using contour integration,

$$\psi_e(t) = e^{-i(E_e^{(0)} + \Delta^{(1)})t} e^{-(\Gamma^{(1)}/2)t} |e\rangle|0\rangle, \quad (7)$$

where the lowest-order self-energy is decomposed into its real and imaginary parts  $\Delta^{(1)}$ ,  $\Gamma^{(1)}$ ,

$$\begin{aligned} \Sigma^{(1)}(E_e^{(0)}) &= \Delta^{(1)} - \frac{1}{2}i\Gamma^{(1)} \\ &= \sum_k \frac{|\langle g; |k\rangle H_I |e; 0\rangle|^2}{\omega_0 - \omega_k + i\epsilon}. \end{aligned} \quad (8)$$

Note that the wave function  $\psi_e(t)$  is damped owing to the emission of a photon and transition to the ground state and that the spectral distribution of the emitted photon is Lorentzian, centered at  $\omega_k = \omega_0 + \Delta^{(1)}$  [owing to the approximation of replacing  $\Sigma^{(1)}(E)$  by  $\Sigma^{(1)}(E_e^{(0)})$ ], and has a width  $\frac{1}{2}\Gamma^{(1)}$ . Clearly the linewidth of the photon,  $\frac{1}{2}\Gamma^{(1)}$ , is an observable, as the experiment can be repeated on a single-excited-atom system and the frequency distribution of the emitted light determined, while the shift  $\Delta^{(1)}$  is not accessible to measurement, as only the center frequency  $\omega_0 + \Delta^{(1)}$  can be determined. This corresponds to the presence of the quantized electromagnetic field, whose interaction with the excited atom cannot be turned off.

Next consider the case  $N=2$ . The starting Hamiltonian is now

$$H_0 = \frac{1}{2} \omega_0 \sum_{i=1}^2 \sigma_z^{(i)} + \sum_k \omega_k a_k^\dagger a_k, \quad (1')$$

$$H_I = \sum_{i=1}^2 \sum_{k\lambda} (\vec{\epsilon}_\lambda \cdot \vec{p}) (\sigma_+^{(i)} + \sigma_-^{(i)}) (a_k e^{i\vec{k} \cdot \vec{R}_i} - a_k^\dagger e^{-i\vec{k} \cdot \vec{R}_i}).$$

A large number of workers have considered this system,<sup>3, 5, 9, 25-28</sup> and its interesting properties. In an early paper, Hamilton<sup>31(a)</sup> used quantum electrodynamics (QED) to show that the interaction energy of two identical atoms, one excited and the other in its ground state, is causal, i. e., that the retardation of the interaction potential plays a crucial role in describing the effect of an excited atom on an unexcited one in its neighborhood. Interesting consequences of the retarded nature of the interaction and the description of the field in terms of QED were derived by Casimir and Polder<sup>29(a)</sup> and later by Dzyaloshinskii,<sup>32</sup> who showed that the effective interaction of two neutral polarizable particles falls off  $\sim 1/R^7$  ( $R$  separation distance) not as expected,  $\sim 1/R^6$ , from the static part of the dipole-dipole interaction energy as a consequence of the retarded nature of virtual photons coupling the particles.

Again the renormalization point of view and the complimentary concepts of propagators (Green's function) and self-energy are used to discuss the

system of two identical two-level systems. In particular, consider the initial state at  $t=0$  of *one* excitation for the system (i. e., either molecule 1 or 2 excited, with the other unexcited and no photons present). Our interest lies in the time evolution ( $t > 0$ ) and spectral properties of this system.

In Fig. 2 the lowest-order Feynman diagrams are shown diagrammatically. The first diagram [Fig. 2(a)] shows the independent emission of one photon by either molecule 1 or 2, while the next diagram [Fig. 2(b)] exhibits the possibility of transferring the excitation from 1  $\rightarrow$  2 and vice versa. It is the latter process, when summed to all orders [Fig. 2(c)] which leads to an interaction energy  $\Sigma^{(2)}(E)$  (self-energy of the two-particle system), which renormalizes its eigenvalue spectrum. Note, that other possible diagrams shown in Fig. 2(d) have not been included, but the recipe of including *resonant* diagrams to infinite order has been followed. The connection of this approximation to the Wigner-Weisskopf approach will be discussed in a separate publication.<sup>31(b)</sup>

As an aside, the reader is reminded that the same process of resonant energy exchange between neighboring atoms, ions, or molecules is well known in solid-state and chemical physics, where the resultant splitting of degenerate (in the absence of coupling) energy levels is referred to as

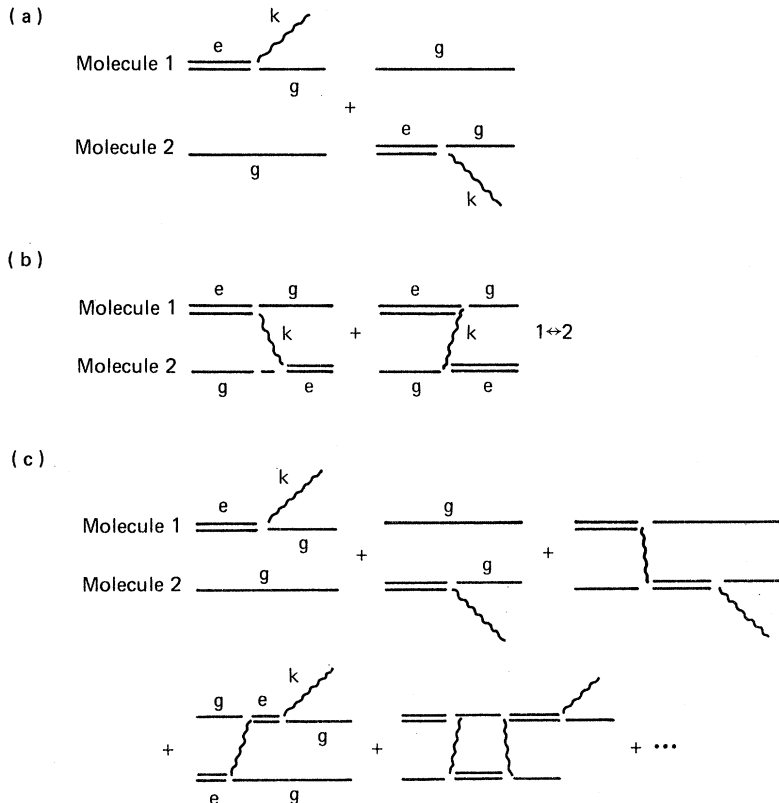


FIG. 2. Lowest-order self-energy  $\Sigma^{(2)}(E)$  for  $N=2$  and decay amplitude. (a) Uncorrelated decay (independent molecule model) for  $N=2$  system; (b) lowest-order self-energy  $\Sigma^{(2)}(E)$  (photon exchange); (c) decay of renormalized  $N=2$  system from superradiant state.

Davydov splitting.<sup>33</sup> In solid-state physics, the presence of lattice periodicity leads in addition to dispersion of the appropriate collective excitation mode of the atoms, ions, or molecules forming the crystal.<sup>34</sup>

In Appendix A the details of calculating the contribution of Fig. 2(b) is given and it is found that

$$\Sigma^{(2)}(E) = k^3 e^{-i\kappa} \left[ \frac{(\vec{p}_1 \cdot \vec{R})(\vec{p}_2 \cdot \vec{R})}{R^2} \left( \frac{1}{\kappa} - \frac{3i}{\kappa^2} - \frac{3}{\kappa^3} \right) + (\vec{p}_1 \cdot \vec{p}_2) \left( -\frac{1}{\kappa} + \frac{i}{\kappa^2} + \frac{1}{\kappa^3} \right) \right]; \quad (9)$$

$E = ck$ ;  $\kappa = kR$ ;  $\vec{p}_{1,2} = -e \langle e_{1,2} | \vec{x} | g_{1,2} \rangle$ ;  $|e_{1,2}\rangle$ ,  $|g_{1,2}\rangle$  are the excited and ground states of molecules 1 and 2; and  $\vec{R} = \vec{R}_1 - \vec{R}_2$  ( $R = |\vec{R}|$ ),  $\vec{R}_{1,2}$  are the position vectors of molecules 1 and 2.

In analogy to the  $N=1$  case, the self-energy  $\Sigma^{(2)}(E)$  in Eq. (9) is complex. A significant difference, however, arises in the interpretation of its real part, the shift  $\Delta^{(2)}(E)$ . To start the discussion of the difference, assume that the single-molecule propagators (solid lines in Fig. 2)  $G_{g,e}^{(1)}(i)$  ( $i=1, 2$ ) for ground and excited states of the individual particles 1 and 2 are expressed in terms of the renormalized diagrams discussed earlier for  $N=1$ .  $\Delta^{(2)}(E)$  is therefore the additional shift of the two-particle system arising from additional energy-exchange diagrams or the many-body nature of the state wave function. It is analogous to the Lamb shift of a 1s electron due to the Coulomb field of the nucleus, which modifies the purely radiative self-energy of an electron in the absence of the nucleus. Here it is the retarded-dipole field of the excited part of the system which modifies the individual self-interactions of particles 1 and 2. Equivalently, the two-particle system can be described as a *single*-quantum system, and for two identical molecules the photon emitted by the excited molecule has a finite probability of being reabsorbed by the same molecule or exchange ground and excited states by propagating across the intervening space and exciting the unexcited molecule. Note, that the simple static picture of an instantaneous dipole-dipole interaction is strongly modified by the consideration of the *finite* propagation velocity of the photon, leading to a *retarded* interaction. Furthermore, as pointed out by Stephen,<sup>12</sup> it is possible to speak of an interaction energy between the two molecules only if the appropriate state is quasistationary, i. e., the photon (= quantum of excitation energy) is exchanged many times between the two molecules. This paper also points out that despite the fact that we talk about exchanging photons between the two molecules, the interaction energy contains terms which are not transverse to the propagation vector  $\vec{k}(\parallel \vec{R}_{12})$ , which implies that the photons exchanged

still have longitudinal parts arising from keeping the near-field contribution together with the radiation-field (far-field) part of the interaction potential. The experimental observation of a photon, emitted from the singly excited two-molecule system, corresponds to the absorption of a *transverse* (real) photon by some photodetector far from the radiation source. Nevertheless, the center frequency and spectral distribution of the observed photon in such an experiment reflect the *renormalized* eigenvalues of the two-molecule system and, in particular, the shift  $\sim \Delta^{(2)}(E)$  from the single-molecule-center frequency should be directly observable.

This is partially borne out by the experiments carried out by Drexhage *et al.*<sup>35,36</sup> on the angular distribution and fluorescence decay time of  $\text{Eu}^{++}$  chelates deposited at well-controlled distances  $d < \lambda_{\text{fluor}}$  from a mirror. The relationship of these experiments to the two-molecule system has been discussed in an earlier publication<sup>25</sup> and good agreement with experiment arrived at, considering the approximations made. The experimental data on the dependence of the inverse-fluorescence decay time on distance from the mirror agreed with a suitably averaged imaginary part  $\Gamma^{(2)}(E)$  of the self-energy  $\Sigma^{(2)}(E)$ . The shift of the fluorescence-center frequency was not expected by the experimentalists and not actually searched for. The presence of other bands in the vicinity of the transition studied ( ${}^5D_0 \rightarrow {}^7F_2$ ;  $\lambda_{\text{fluor}} = 6130 \text{ \AA}$ ) and the onset of energy transfer to the mirror for the small distances ( $< 20 \text{ \AA}$ ) required to give an observable shift may make its experimental detection difficult.<sup>36(b)</sup>

However, the known theoretical expression<sup>3</sup> of the lowest-order two-particle self-energy  $\Sigma^{(2)}(E)$  given in Eq. (6) will be used to explain the approach based on the analytic properties of  $\Sigma^{(2)}(E)$  in the upper half-plane ( $E = E_R + iE_I$ ,  $E_I \geq 0$ ). In order to simplify the discussion,  $\Sigma^{(2)}$  is decomposed into a longitudinal and transverse part,  $\Sigma^{\parallel}$  and  $\Sigma^{\perp}$ , according to the decomposition of the transition dipoles  $\vec{p}_1, \vec{p}_2$  into components along  $\vec{R}$  (longitudinal) and at right angles to it (transverse), anticipating a photon measured with  $\vec{k} \parallel \vec{R}$ :

$$\begin{aligned} \vec{p}_{1,2} &= p_{1,2}^{\parallel} \vec{n} + p_{1,2}^{\perp} \vec{t}, \\ \vec{n} &= \vec{R}/R, & \vec{t} &= \vec{R}_1 \times \vec{n}/R_1, \\ p_{1,2}^{\parallel} &= (\vec{p}_{1,2} \cdot \vec{n}), & p_{1,2}^{\perp} &= \vec{p}_{1,2} \cdot \vec{t}; \end{aligned} \quad (10)$$

for  $\Sigma^{\parallel}$  and  $\Sigma^{\perp}$  it is found that

$$\Sigma^{(2)\parallel}(E) = k^3 p_1^{\perp} p_2^{\perp} e^{-i\kappa} (1/\kappa + i/\kappa^2 + 1/\kappa^3), \quad (9a)$$

$$\Sigma^{(2)\perp}(E) = 2k^3 p_1^{\parallel} p_2^{\parallel} e^{-i\kappa} (i/\kappa^2 + 1/\kappa^3). \quad (9b)$$

The subsequent discussion is now specified to a

specific molecular configuration of the transition dipoles parallel to each other and  $\vec{n}$ , i. e.,

$$\vec{p}_{1,2} = p_{1,2} \vec{n}.$$

Suppose that one is given *only* the imaginary part of (9a), i. e.,

$$-\text{Im} \Sigma^{(2)''}(E) = 3\gamma_0 \left( \frac{\cos \kappa}{\kappa^2} - \frac{\sin \kappa}{\kappa^3} \right),$$

$$\gamma_0 = \frac{2}{3} k^3 |p_{1,2 \max}|^2. \quad (11)$$

Here  $\gamma_0$  is the free-space isolated-molecule decay rate ( $\equiv$  width of spectral distribution of the emitted quantum). Now, it is proposed that the analyticity of the self-energy  $\Sigma^{(2)}(E)$  be used to calculate the real part of the self-energy from the given information  $[-\text{Im} \Sigma^{(2)''}(E)]$ .  $\Sigma^{(2)}(E)$  is the Fourier transform of the causal self-energy  $\Sigma^{(2)}(t)$ ,

$$\Sigma^{(2)}(E) = (1/2\pi) \int_{-\infty}^{\infty} e^{iEt} \Sigma^{(2)}(t) dt, \quad (12)$$

$$\Sigma^{(2)}(t) = \begin{cases} \Sigma^{(2)}(t) & \text{for } t \geq 0 \\ 0 & \text{for } t < 0. \end{cases} \quad (12a)$$

Equation (12a) can be shown to hold by considering the time evolution of the two-molecule system prepared such that at  $t=0$  there is *one* excitation present for the system. In fact, if it is assumed that a particular molecule, say molecule 1, is excited and molecule 2 is unexcited, Hamilton<sup>31</sup> has shown that the decay proceeds as for the two independent molecules for times  $t < R/c$ , i. e., until the radiation from molecule 1 has propagated to molecule 2. It follows from (12) that  $\Sigma^{(2)}(E)$  is analytic in the upper-half complex energy plane, and therefore a Cauchy formula can be written for it as a function

$$\Delta^{(2)''}(E) = \frac{3}{4\pi} \int_{-\infty}^{\infty} \gamma_0(E') dE' \left( \frac{1}{E' - E - i\epsilon} + \frac{1}{E' - E + i\epsilon} \right)$$

$$\times \left[ e^{i\beta E'} \left( \frac{1}{(E'\beta)^2} + \frac{i}{(E'\beta)^3} \right) + e^{-i\beta E'} \left( \frac{1}{(E'\beta)^2} - \frac{i}{(E'\beta)^3} \right) \right], \quad (17)$$

which can be evaluated in a straightforward way by the residue theorem as the only singularities occur for  $E' = E + i\epsilon$  and  $E' = E' - i\epsilon$  and the contour can be chosen in the upper half-plane for the terms

$$\Delta^{(2)''}(E) = \frac{3}{2\pi} \gamma_0(E) 2i\pi \left[ \frac{e^{i\beta E}}{2} \left( \frac{1}{(E\beta)^2} + \frac{i}{(E\beta)^3} \right) - \frac{e^{-i\beta E}}{2} \left( \frac{1}{(E\beta)^2} - \frac{i}{(E\beta)^3} \right) \right] = -3\gamma_0 \left( \frac{\sin \kappa}{\kappa^2} + \frac{\cos \kappa}{\kappa^3} \right), \quad (18)$$

which is, as expected, the real part of Eq. (9b).

In complete analogy,  $\Gamma^{(2)\perp}(E)$  could be used as input information and the dispersion relation used

of complex  $z$ , namely,

$$\Sigma^{(2)}(z) = \frac{1}{2\pi i} \int_C \frac{\Sigma^{(2)}(z') dz'}{z' - z}. \quad (13)$$

The physical self-energy  $\Sigma^{(2)}(E + i\epsilon)$  is defined just above the real axis,

$$\Sigma^{(2)}(E + i\epsilon) = \Delta^{(2)}(E) - \frac{1}{2} i \Gamma^{(2)}(E), \quad (14)$$

and the standard identity

$$\frac{1}{E' - E - i\epsilon} = P \frac{1}{E' - E} + i\pi \delta(E' - E) \quad (15)$$

is used.

The contour  $C$  is chosen as along the real axis  $-\infty \leq E' < \infty$  and a semicircle at infinity in the upper half-plane. As the contribution along the latter part of the contour vanishes, one finds from (13), by equating real parts using (14) and (15), that

$$\Delta^{(2)''}(E) = \frac{-1}{\pi} P \int_{-\infty}^{\infty} \frac{dE' \Gamma^{(2)''}(E')}{E' - E}, \quad (13a)$$

which is a Kramers-Kronig relation (Hilbert transform) between  $\Delta^{(2)''}$  and  $\Gamma^{(2)''}$ .<sup>37</sup> Since it has been assumed that the integrand  $\Gamma^{(2)''}(E')$  is to be given analytically by Eq. (11), one is left with evaluating the principal-value integral in (13a). Using the identity

$$P \frac{1}{E' - E} = \frac{1}{2} \left( \frac{1}{E' - E - i\epsilon} + \frac{1}{E' - E + i\epsilon} \right) \quad (16)$$

and separating terms  $\sim e^{i\beta E'}$  and  $\sim e^{-i\beta E'}$  ( $\beta = R/c$ ) in the integrand arising from the  $\sin k'R$  and  $\cos k'R'$  parts of  $\Gamma^{(2)''}(E')$ , the following is obtained [see also Ref. 9, second paper, Eq. (21) for a different derivation]:

$\sim e^{i\beta E'}$  and in the lower half-plane for the terms  $\sim e^{-i\beta E'}$ . The apparent singularities at  $E' = 0$  do not contribute as the integrand is regular at  $E' = 0$ . Using the residue theorem, one obtains

to find  $\Delta^{(2)\perp}(E)$ . It has been demonstrated, therefore, for the case of the simplest superradiant system  $N=2$ , how the knowledge of the imaginary part

of the self-energy allows one to calculate the shift  $\Delta^{(2)}$  of the eigenfrequencies of the coupled two-molecule system, which is, in principle, a measurable effect.

### III. GENERALIZATION TO $N \gg 1$ MOLECULE CASE

Dicke<sup>1</sup> has discussed the properties of  $N \gg 1$  two-level molecules in detail and, in particular, pointed out the dramatic consequences of cooperative behavior for the case of  $N$  molecules confined in a volume  $V$ , such that  $V < \lambda^3$ , and the case of a cylindrical column of small Fresnel number  $a^2/\lambda L \ll 1$  ( $a$  radius of cylinder,  $L$  its length). Exploiting the isomorphism of the density matrix for a two-level atom and a spin- $\frac{1}{2}$  particle, he has constructed eigenfunctions  $|\nu, m\rangle$  of the pseudo-angular-momentum operator

$$R^2 = \sum_{j=1,2,3}^N r_j^{(j)2};$$

$$r_1^{(j)} = \sigma_x^{(j)}, \quad r_2^{(j)} = \sigma_y^{(j)}, \quad r_3^{(j)} = \sigma_z^{(j)}$$

and

$$M_z = \sum_{i=1}^N r_3^{(i)}$$

with eigenvalues  $\nu$ , the cooperation number, and  $m$ , the molecular energy. In terms of these eigenstates, he finds the radiation rate to be given by

$$\gamma_{\nu m}^{\text{Dicke}} = (\nu + m)(\nu - m + 1)\gamma_0$$

$$= \frac{1}{4}N^2\gamma_0 \quad \text{for } \nu = \frac{1}{2}N, \quad m = 0. \quad (19)$$

This result was derived by first-order perturbation theory, i. e., computing the time-evolution of the fully inverted state ( $\nu = m = \frac{1}{2}N$ ) due to the interaction operator (in electric dipole approximation):

$$H_I = \sum_{j=1}^N g_k (\epsilon_+ r_+^{(j)} a_k^\dagger e^{-i\vec{k} \cdot \vec{R}_j} + \epsilon_- r_-^{(j)} a_k e^{i\vec{k} \cdot \vec{R}_j})$$

$$= \sum_k g_k (a_k^\dagger R_-^{(k)} \epsilon_+ + a_k R_+^{(k)} \epsilon_-), \quad (20)$$

with  $g_k = p(\omega k/Vc)^{1/2}$ ,  $\epsilon_{+,-} = \epsilon_x \pm i\epsilon_y$ ,  $r_{+,-}^{(j)} = (1/\sqrt{2})(\sigma_x^{(j)} \pm i\sigma_y^{(j)})$ ,

$$R_{-+}^{(k)} = \sum_{j=1}^N r_{-+}^{(j)} e^{i\vec{k} \cdot \vec{r}_j}$$

whose matrix elements are the standard angular-momentum factors ( $\vec{k}$  is considered fixed, corresponding to preparation of the sample by a plane-wave pulse with  $\vec{k}$  parallel to the cylinder axis)<sup>1</sup>:

$$R_-^{(k)} |\nu, m\rangle = [(\nu + m)(\nu - m + 1)]^{1/2} |\nu, m - 1\rangle.$$

As first-order perturbation theory was used to calculate the spontaneous-emission rate, the effect of renormalization of the superradiant states  $|\nu, m\rangle$  was not considered. Later work by Fain,<sup>2</sup> Ernst

and Stehle,<sup>5</sup> and in particular by Arecchi, Kim, and Smith,<sup>27,28</sup> pointed out the necessity of taking the different renormalization of the  $|\nu, m\rangle$  states into account. The latter authors<sup>28</sup> gave an example of striking consequences of renormalization for the fully excited  $N=2$  system.

Our interest lies in the spectral properties of the superradiant pulse, specifically its detection as a shift from the free two-level separation frequency  $\omega_0 = E_e - E_g$ , which is preserved in the Dicke treatment, in which the effect of the radiation field back on the  $N$  molecules is neglected.

Note that Eq. (19) for sufficiently large  $N$  quickly leads into the realm of science fiction<sup>38</sup> ("optical bomb"). This is due to the fact that the number  $N$  of molecules contributing to cooperative spontaneous emission has certain built-in limitations and cannot simply be taken from Dicke's work, which utilized first-order perturbation theory and the usual averaging over a few cycles. Instead, Arecchi and Courtens<sup>13</sup> start from the observation already contained in Hamilton's<sup>31</sup> work, that cooperative behavior in the superradiant system sets in, after the photon emitted from one of the atoms has reached the other atom(s). That is, the retarded nature of the interaction plays a crucial role for the timing and length of the cooperative behavior.

The two relevant parameters for the pencil-like geometry are briefly presented, namely,  $N_c$ , the cooperation number, and  $\tau_c = \pi/\gamma_c$ , the cooperation time. ( $\gamma_c$  is the modified Dicke cooperative decay rate per molecule for  $N_c$  molecules.) The superradiant coherence length  $l_c = c/\gamma_c$  is simply the linear extent of the sample along the cylinder axis ( $\parallel$  to the propagation direction of the superradiant emission) over which the  $N_c$  molecules superradiate. From Ref. 13,

$$\gamma_c = \frac{1}{4} N_c \gamma_0 (\lambda^2/A), \quad (21a)$$

$$N_c = l_c A \rho, \quad (21b)$$

where  $\gamma_0 = \frac{2}{3} p^2 k^3$  is the free-space single-molecule decay rate ( $p = |p_{\text{max}}|$  is the maximum value of the transition dipole),  $\lambda^2/A$  is the element of solid angle subtended by the superradiant emission (diffraction limited), and  $\rho$  is the molecular density in the sample. For the case of an inhomogeneously broadened line, (21b) is modified to  $l_c = cT_2^*$ , where  $T_2^*$  is the inverse inhomogeneous linewidth. For the homogeneously broadened line it is found by solving (21a) and (21b) that

$$\gamma_c = \frac{1}{2} \lambda (c\rho\gamma_0)^{1/2}, \quad (22)$$

$$N_c = \frac{2A}{\lambda} \left( \frac{\rho c}{\gamma_0} \right)^{1/2}.$$

As the Dicke rate [Eq. (19)] for the  $N$ -molecule system corresponds by the same argument as made in Sec. II to the imaginary part of the  $N$ -molecule

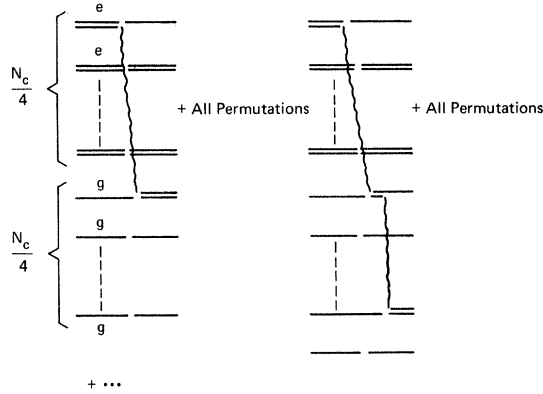


FIG. 3. Schematic  $N \gg 1$  molecular self-energy  $\Sigma^N(E)$  for superradiant state  $|r = \frac{1}{2}N_c m = 0\rangle$ .

self-energy  $\Sigma^{(N)}(E)$ , the modification (21) to determine an effective  $\Sigma^{(N)}(E)$  is considered. We propose to use  $\gamma_c(E)$  as the phenomenological imaginary part  $\Gamma^{(N)}(E)$  of a causal  $N$ -molecule self-energy  $\Sigma^{(N)}(E)$  and use, in analogy to the case  $N=2$ , the dispersion relation of Eq. (13a) to calculate an effective shift  $\Delta^{(N)}(E)$ ,

$$\Delta^{(N)}(E) = \frac{-1}{\pi} P \int_{-\infty}^{\infty} \frac{\Gamma^{(N)}(E') dE'}{E' - E}. \quad (23)$$

From a many-body point of view, the  $N$ -molecule self-energy  $\Sigma^{(N)}(E)$  is a complicated object, and its structure is indicated schematically in Fig. 3. The state, which has the most dramatic manifestations of cooperative behavior, is  $|r = \frac{1}{2}N m = 0\rangle$ , corresponding to the total system being in an energy superposition state, or equivalently in the semiclassical model<sup>39</sup> to being rotated by a  $\frac{1}{2}\pi$  pulse into the  $x$ - $y$  plane (with orientation along the positive  $z$  axis, corresponding to complete inversion  $|r = \frac{1}{2}N, m = \frac{1}{2}N\rangle$  and along the negative  $z$  axis corresponding to the ground state  $|r = \frac{1}{2}N, m = -\frac{1}{2}N\rangle$ ).

It is in this and close-lying states  $|r = \frac{1}{2}N, m \sim 0\rangle$  that the system exhibits a macroscopic dipole moment and thus radiates coherently. If one uses the evenness of  $\Gamma^{(N)}(E') = \Gamma^{(N)}(-E')$ , which follows from general arguments,<sup>37</sup> and calculates  $\Delta^N(E)$  from Eq. (23) using (22), then

$$\Delta^{(N)}(E) = -\frac{2E}{\pi} P \int_0^{\infty} \frac{\gamma_c(E') dE'}{E'^2 - E^2}. \quad (24)$$

Before evaluating Eq. (24) several points should be made concerning the principal-value integral, its limits, and the behavior of the integrand. By definition, the value of the principal-value integral depends on non-energy-conserving values  $E' \neq E$  of the integrand  $\Gamma^{(N)}(E')$ . One should consider the fact that the physical dimensions of the system considered limit the contributing frequencies to  $E_{\min} \leq E' \leq E_{\max}$  in the following manner: (a) by assump-

tion the  $N$  molecules are nonoverlapping in space, consequently the highest Fourier component contributing to the dispersion integral (24) is of order  $E_{\max} = 2\pi c/D$ , where  $D$  is a typical molecular diameter; (b) it has been assumed that the cylindrical sample has length  $L$ , and consequently, the lowest Fourier component contributing is of order  $E_{\min} = 2\pi c/L$ . One, therefore, replaces the limits of integration in (24) by the low- and high-frequency cutoffs  $E_{\min}$  and  $E_{\max}$ , respectively. The resulting principal-value integral then gives to lowest order in  $\lambda/L$ ,  $D/\lambda \ll 1$  [see Appendix B, Eq. (B7)],

$$\Delta^{(N)}(E) \simeq \frac{2}{\pi} \gamma_c(E) \left\{ \ln\left(\frac{\lambda}{L}\right) + \frac{1}{2} \left[ \left(\frac{\lambda}{L}\right)^2 - \left(\frac{D}{\lambda}\right)^2 \right] \right\}, \quad (25)$$

which disagrees with the earlier estimates of Fain<sup>32</sup> and Arecchi *et al.*<sup>27</sup> Note, however, that in using the expression for the self-consistent superradiant rate  $\gamma_c$ , the free-space single-molecule rate  $\gamma_0$  appears. Fermi's golden rule gives

$$\gamma_0 = 2\pi |\dot{p}_{eg}|^2 \rho_f(k) = \frac{2}{3} \dot{p}^2 k^3,$$

where

$$\rho_f = 2 \frac{V}{(2\pi)^3} \int \frac{d^3 k'}{V} |k'| \delta(\omega_0 - \omega_k') \left( 1 - \frac{(\vec{k}' \cdot \vec{p})^2}{|k'|^2 |p|^2} \right) \quad (26)$$

is the photon density of states at  $\omega_k = E_e - E_g$ ,  $\dot{p}^2 = e^2 |\langle e | x | g \rangle|_{\max}^2$  is the square of the maximum value of the electric-transition-dipole matrix element. As  $\gamma_c(E')$  is considered here as a function of  $E'$ , the  $E'$  dependence of  $\gamma_0 \equiv \gamma_0(E')$  should be kept in the dispersion integral. This, of course, weights the cutoff frequencies  $E_{\min}$ ,  $E_{\max}$  differently and we find [Appendix B, Eq. (B14)]

$$\Delta^{(N)}(E) = \frac{2}{\pi} \gamma_c(E) \left[ \frac{\pi}{2} + \left(\frac{\lambda}{L}\right)^{1/2} - \left(\frac{D}{\lambda}\right)^{1/2} \right]. \quad (27)$$

Obviously, the shift obtained crucially depends on which of these points of view is the correct one. As the dispersion approach relates the off-resonant behavior of one quantity (the width) to the resonant value of the other (the shift), it is felt that the neglect of the frequency dependence of  $\gamma_0(E')$  is unjustified and that Eq. (27) is the correct expression for the shift of the transition frequency.

For the case of inhomogeneous broadening, the modified expression

$$\gamma_c = \frac{1}{4} c T_2^* \rho \gamma_0 \lambda^2 \quad (28)$$

has to be used to account for the smaller [by a factor  $\sim (\gamma_c/\gamma_D) (T_2^* \pi/\gamma_D)$ ,  $\gamma_D$  Doppler width] number of molecules available for cooperative behavior in the superradiant emission. Proceeding as before by neglecting the frequency dependence of  $\gamma_0$ , the shift [Appendix B, Eq. (B10)] is found to be

$$\Delta^{(N)}(E) = \frac{2}{\pi} \gamma_c(E) \left( \frac{L}{\lambda} - \frac{\lambda}{L} \right), \quad (29)$$



TABLE I. Typical values for the superradiant level shift  $\Delta^{(N)}(E)$  for a molecular gas pumped by the  $\lambda=10.6\text{-}\mu$  CO<sub>2</sub> line. The predicted shift for the experiment proposed is  $5.8 \times 10^6 \text{ sec}^{-1}$  [case (b), inhomogeneous broadening].

	$\gamma_0$ (sec <sup>-1</sup> )	$\gamma_D$	$\rho$ (cm <sup>-3</sup> )	$D$	$\lambda$ (cm)	$L$	$\gamma_c(E)$	$\Delta^{(N)}(E)$ (sec <sup>-1</sup> )	$\Delta^{(N)}(E)$
Homogeneous broadening	$10^2$	0	$10^8$	$2 \times 10^{-8}$	$10.6 \times 10^{-4}$	10	$8.5 \times 10^6$	$-4.9 \times 10^7$	$8.5 \times 10^6$
Inhomogeneous broadening	$10^2$	$10^8$	$10^8$	$2 \times 10^{-8}$	$10.6 \times 10^{-4}$	10	$8.4 \times 10^5$	$5.0 \times 10^9$	$5.8 \times 10^6$

essentially diverging linearly with sample size  $L$ . Taking the frequency dependence of  $\gamma_0(E')$  into account [note that for the case  $N=2$ , Eq. (17) implied the necessity for this step],

$$\Delta^{(N)}(E) = \frac{2}{\pi} \gamma_c(E) \left\{ \ln \frac{\lambda}{D} + \frac{1}{2} \left[ \left( \frac{\lambda}{L} \right)^2 - \left( \frac{D}{\lambda} \right)^2 \right] \right\}, \quad (30)$$

which is used to predict a value of 5.8 MHz for the shift for the set of parameters specified in Table I. Note that the width of the superradiant pulse for inhomogeneous broadening is of order  $\tau_c = \pi/\gamma_c = 3.7 \times 10^{-6}$  sec, and that assuming the shift slowly varying over times comparable to  $\tau_c$ , a sufficient number of beats ( $\sim 20$ ) between the laser field at  $\omega_L$  and the superradiant emission at  $\omega_{SR} = \omega_L + \Delta^{(N)}(E)$  should occur to be observable.

#### IV. PROPOSED TRANSIENT OPTICAL EXPERIMENT FOR DETECTION OF SUPERRADIANT SHIFT $\Delta^{(N)}(E)$

In Sec. III, it was shown how the self-consistent superradiant radiation rate can be considered to define an effective  $N$ -molecule self-energy and a resultant level shift in the superradiant spectrum was calculated. Although the calculation directly applies only to the most superradiant state  $|r = \frac{1}{2}N_c, m=0\rangle$ , or rather its self-consistent modification, it is argued that similar arguments hold for the set of states  $|r = \frac{1}{2}N_c, m \ll \frac{1}{2}N_c\rangle$  by analogy. The photons emitted, while the system evolves from the superradiant ( $m \ll N_c \gg 1$ ) to the ground state ( $m = -\frac{1}{2}N_c$ ) will be shifted by  $\Delta^{(N)}(\omega_0)$  and have the frequency

$$\omega_k = \omega_0 + \Delta^{(N)}(\omega_0) \quad (31)$$

and it is proposed that this shift be detected by heterodyning the superradiant field with a cw laser field.

The experimental arrangement proposed is based on the recent development of an elegant transient optical method by Brewer and Shoemaker for the observation of nonlinear spectroscopic and interference effects<sup>23</sup> in samples of molecular gases excited cw by a CO<sub>2</sub> laser. The 10.6- $\mu$  CO<sub>2</sub> laser line resonantly excites a particular velocity subgroup of a vibrational-rotational transition in the gas, in which the orbital degeneracy has been removed by application of an external Stark field.<sup>23</sup>

Utilizing a rapidly variable electronic switch, the Stark field can be suddenly changed at  $t=0$ , moving the originally pumped subgroup of molecules out of resonance and a new group of molecules into resonance. By a suitable choice of laser operating frequency and Stark field, the hole burned into the Doppler profile can be shifted from close to line center ( $v_0 \approx 0$ ) to the far wings ( $v_0 \approx 10^4$  cm sec<sup>-1</sup>), corresponding to a small number of molecules. The originally excited group of molecules will closely resemble a superradiant system and return to its ground state by emitting a pulse of superradiant light at frequency  $\omega_k = \omega_0 + \Delta^{(N)}(\omega_0)$ . The non-adiabatic nature of the Stark switching leads to a whole set of interesting transient effects,<sup>23</sup> and the one proposed here is a new one<sup>24</sup>: the detection of the superradiant level shift  $\Delta^{(N)}(E)$  as a beat signal  $\sim \cos \Delta^{(N)} t$  with the cw laser field  $\omega_L = \omega_0$ .

A sketch of the proposed experimental setup is given in Fig. 4. A cw CO<sub>2</sub> laser prepares the particular velocity subgroup  $v_0$  of molecules, in whose rest frame the laser frequency is Doppler shifted to line center. At  $t=0$  the additional Stark pulse shifts the laser light out of resonance with the velocity subgroup  $v_0$ , leaving the molecules in coherent superposition states corresponding to  $|r = \frac{1}{2}N_c, m \sim 0\rangle$ . These molecules reflect their coherent preparation by emitting superradiant light with a frequency given by Eq. (31), where  $\omega_0 = \omega_L + \Delta_s$ . It is assumed that the original transition has been between a lower state showing a linear Stark effect and an upper state showing a quadratic Stark effect,<sup>20</sup> where  $\Delta_s = \alpha E^{(S)}$  is the linear Stark shift of the lower state,  $\omega_L$  the laser frequency, and  $E^{(S)}$  the additional Stark field applied at  $t=0$ . The total shift  $\Delta^T = \Delta_s + \Delta^{(N)}(E)$ , where  $\Delta_s$  is the Stark shift and  $\Delta^{(N)}(E)$  the superradiant shift, can be observed directly as a beat frequency in a heterodyne detector for sufficiently short times ( $< 10^{-6}$  sec).

Typical numbers for a molecular gas for an experiment are given in Table I. A value of  $\gamma_c \approx 0.84$  MHz and a shift of  $\Delta^N \sim 5.8$  MHz is found. It is pointed out that it seems crucial to reduce the present switching time of  $\sim 30$  nsec of the Stark pulse by about an order of magnitude to avoid smearing out the effect. Also, the detection of the beat over not much more than a few cycles ( $\Delta t$

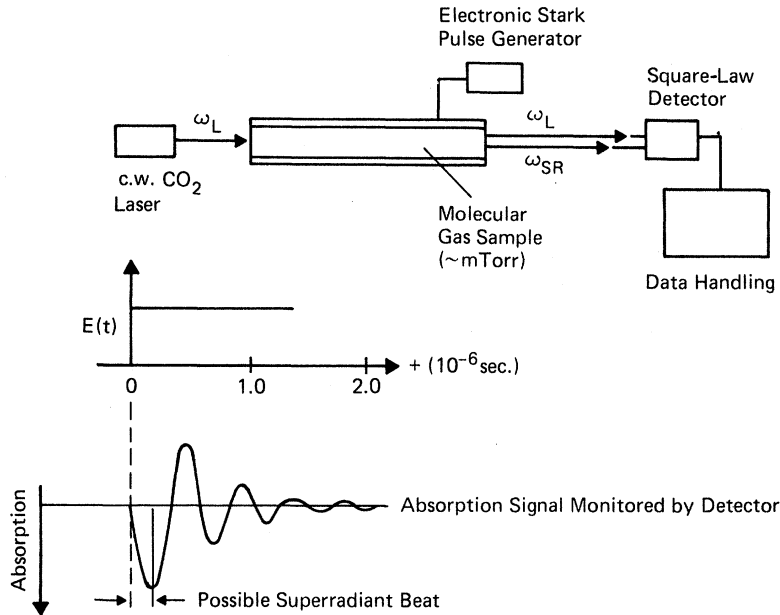


FIG. 4. Proposed transient optical experiment.

$\sim 1/5.8 \times 10^6 = 1.7 \times 10^{-7}$  sec) is not a simple task. Nevertheless we believe that it should be possible to observe the effect in the proposed configuration.

#### V. SUMMARY AND CONCLUSIONS

It has been shown how to use renormalized perturbation theory to discuss the behavior of  $N$  identical two-level molecules coupled to the radiation field. In particular, the concentration has been on the  $N$ -particle self-energy  $\Sigma^{(N)}(E)$ , which arises from the coupling and modifies the eigenfrequencies and width of the emitted photons. The Hilbert transform relations between the real and imaginary parts of  $\Sigma^{(N)}(E)$ ,  $\Delta^{(N)}(E)$ , and  $\Gamma^{(N)}(E)$  have been defined, and these dispersion relations employed to calculate the shift function for the familiar case  $N=2$ . Then the self-consistency argument of Arecchi and Courtens<sup>13</sup> was used to construct an effective  $N$ -molecule self-energy function from its imaginary part  $\gamma_e(E)$  and the resulting shift calculated. Some interesting consequences of the nature of the dispersion relation in terms of its dependence on low- and high-frequency cutoffs, determined by the physics of the system considered, were brought out and the functional dependence of the integrand on the dispersion variable away from resonance discussed. Finally, a possible transient optical experiment for the observation of the shift is proposed and representative values for the relevant parameters are given. The  $N$ -molecule shift  $\Delta^{(N)}(E)$  is a dramatic consequence of higher-order radiative corrections in the particular many-body context of superradiance and thus confirms the present understanding and use of quantum electrodynamics.

#### ACKNOWLEDGMENTS

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#### APPENDIX A

$\Sigma^{(2)}(E)$  is calculated by using standard time-dependent perturbation theory<sup>30</sup> (see also Ref. 3) for the S-matrix element

$$S_{12} \equiv \langle 2e, 1g; O_k | S_{op}(\infty, 0) | 2g, 1e; O_k \rangle,$$

with

$$S_{op}(t_1, t_2) \equiv T \left\{ \exp \left[ -i \int_{t_2}^{t_1} H_1(t') dt' \right] \right\}. \quad (A1)$$

One finds to second order in  $H_1$  [Fig. 2(b)],

$$S^{(2)} = -2\pi i \delta(\omega_0^{(1)} - \omega_0^{(2)}) \Sigma^{(2)}(E), \quad (A2)$$

and  $\Sigma^{(2)}(E)$  is given by the expression

$$\Sigma^{(2)}(E) = \sum_n \frac{\langle 1g, 2e; O_k | H_I | n \rangle \langle n | H_I | 1e, 2g; O_k \rangle}{-E_n + i\epsilon}. \quad (A3)$$

The initial state for the  $N=2$  superradiant system is given by  $|i\rangle = |1e, 2g; O_k\rangle$  and the final state by  $|f\rangle = |2e, 1g; O_k\rangle$ . For the intermediate state  $n$ , the two states

$$|n\rangle = |1g, 2g; 1_k\rangle \quad \text{with energy } E_n = -\omega_0 + \omega_k,$$

$$|n'\rangle = |1e, 2e; 1_{k'}\rangle \quad \text{with energy } E_{n'} = \omega_0 + \omega_{k'}$$

are taken corresponding to the two time-ordered diagrams [Fig. 2(b)]. In the first one of these,

molecule 1 in the excited state emits a photon and returns to the ground state, while molecule 2 remains in the ground state until it absorbs the emitted photon and goes to the excited state. In the second diagram, molecule 2 emits a photon  $\omega_k$  and goes to the excited state, while molecule 1 stays in the excited state until it absorbs the photon  $\omega_k$  and goes to the ground state. Obviously, photon  $\omega_k$  is an unphysical photon (negative frequency), but necessary by crossing symmetry.<sup>30,40</sup>

Using Eq. (1a) for the interaction Hamiltonian  $H_1$  in (A3), defining the matrix elements

$$\begin{aligned} \langle O_k; 2e | H_I | 2g; 1_k \rangle &= \vec{\epsilon} \cdot \vec{p}_2 e^{-i\vec{k} \cdot \vec{R}_2}, \\ \langle 1_k; 1g | H_I | 1e; O_k \rangle &= \vec{\epsilon} \cdot \vec{p}_1 e^{i\vec{k} \cdot \vec{R}_1}, \end{aligned} \quad (\text{A4})$$

writing the intermediate-state sum  $n$  as a three-dimensional integral over photon momenta  $\vec{k}$ , and summing over polarization vectors  $\epsilon_\lambda$  with  $\lambda = \lambda_1^{(k)}, \lambda_2^{(k)}$ , one obtains

$$\begin{aligned} \Sigma^{(2)}(E) &= \int d^3k \sum_\lambda \left( \frac{(\vec{\epsilon}^{(\lambda)} \cdot \vec{p}_2)(\vec{\epsilon}^{(\lambda)} \cdot \vec{p}_1)}{\omega_0 - \omega_k + i\epsilon} e^{i\vec{k} \cdot \vec{R}} \right. \\ &\quad \left. + \frac{(\vec{\epsilon}^{(\lambda)} \cdot \vec{p}_1)(\vec{\epsilon}^{(\lambda)} \cdot \vec{p}_2)}{-\omega_0 - \omega_k + i\epsilon} e^{-i\vec{k} \cdot \vec{R}} \right). \end{aligned} \quad (\text{A5})$$

Choosing  $\vec{R}$  as the  $z$  axis in the  $\vec{k}$  integration and performing the polarization sum by the standard identity

$$\sum_\lambda \epsilon_\alpha^{(\lambda)} \epsilon_\beta^{(\lambda)} = \delta_{\alpha,\beta} - k_\alpha k_\beta / k^2 \quad (\text{A6})$$

leads to

$$\begin{aligned} \Sigma^{(2)}(E) &= \int |k|^3 d|k| d\Omega_k \left( \frac{(\vec{p}_1 \cdot \vec{p}_2) - (\vec{p}_1 \cdot \vec{k})(\vec{p}_2 \cdot \vec{k})}{k^2} \right) \\ &\quad \times \left( \frac{e^{i\vec{k} \cdot \vec{R}}}{\omega_0 - \omega_k + i\epsilon} - \frac{e^{-i\vec{k} \cdot \vec{R}}}{\omega_0 + \omega_k - i\epsilon} \right). \end{aligned} \quad (\text{A7})$$

Expansion of  $e^{\pm i\vec{k} \cdot \vec{R}}$  and  $\vec{k} \cdot \vec{p}_{1,2}$  in Legendre polynomials by

$$e^{i\vec{k} \cdot \vec{R}} = \sum_l i^l (2l+1) j_l(\kappa) P_l(\cos\theta_k)$$

and use of their orthogonality leaves only the  $|k|$  integration to be done. It is easily done by contour integration after a trivial change of variables  $x = c|k|$  giving the desired result

$$\begin{aligned} \Sigma^{(2)}(E) &= k^3 e^{-i\kappa} \left[ \frac{(\vec{p}_1 \cdot \vec{R})(\vec{p}_2 \cdot \vec{R})}{R^2} \left( \frac{1}{\kappa} - \frac{3i}{\kappa^2} - \frac{3}{\kappa^3} \right) \right. \\ &\quad \left. + (\vec{p}_1 \cdot \vec{p}_2) \left( -\frac{1}{\kappa} + \frac{i}{\kappa^2} + \frac{1}{\kappa^3} \right) \right]. \end{aligned} \quad (\text{A8})$$

This is Eq. (9) of the text, used to describe the additional self-energy of the  $N=2$  system.

#### APPENDIX B

The principal-value ( $P$ ) integral for the effective superradiant level shift  $\Delta^{(N)}(E)$  given by [see Eq.

(23) of the text]

$$\Delta^{(N)}(E) = \frac{2E}{\pi} P \int_{E_{\min}}^{E_{\max}} \frac{\Gamma^{(N)}(E') dE'}{E'^2 - E^2} \quad (\text{B1})$$

is considered utilizing the  $N$ -molecule effective imaginary self-energy for the two cases of homogeneous broadening:

$$\Gamma^{(N)}(E) = \gamma_c(E) = \begin{cases} \frac{\pi c}{E} (c\rho\gamma_0)^{1/2} & (\text{homogeneous case}) \\ \pi^3 c^3 \rho \frac{\gamma_0}{\gamma_D} \frac{1}{E^2} & (\text{inhomogeneous case}). \end{cases} \quad (\text{B2})$$

The principal-value integral will be calculated both by (a) letting  $\gamma_0 = \text{const}$  in the dispersion integral (B1), and (b) considering the frequency dependence of  $\gamma_0$ , i. e., differentiating between

$$(a) \gamma_0 = (\text{const})$$

and

$$(b) \gamma_0 = \alpha E^3, \quad \alpha = (2/3c^3)\rho^2. \quad (\text{B3})$$

Case (a)

#### Homogeneous Broadening

First write

$$\Gamma^{(N)}(E') = c_1/E'; \quad c_1 = \pi(c^3\rho\gamma_0)^{1/2} \quad (\text{B4})$$

and define

$$I_1^{(a)}(E) = P \int_{E_{\min}}^{E_{\max}} dx/x(x^2 - E^2). \quad (\text{B5})$$

By definition of the Cauchy principal value,

$$\begin{aligned} I_1^{(a)}(E) &= \lim_{\epsilon \rightarrow 0} \left( \int_{E_{\min}}^{E-\epsilon} + \int_{E+\epsilon}^{E_{\max}} \frac{dx}{x(x^2 - E^2)} \right) \\ &= \frac{1}{E^2} \left[ \ln \frac{\lambda}{L} + \left( \frac{\lambda}{L} \right)^2 - \left( \frac{D}{\lambda} \right)^2 \right]. \end{aligned} \quad (\text{B6})$$

The shift  $\Delta^{(N)}(E)$  is therefore given by

$$\begin{aligned} \Delta^{(N)}(E) &= \frac{2E}{\pi} c_1 I_1^{(a)}(E) \\ &= \frac{2}{\pi} \gamma_c(E) \left\{ \ln \left( \frac{\lambda}{L} \right) + \frac{1}{2} \left[ \left( \frac{\lambda}{L} \right)^2 - \left( \frac{D}{\lambda} \right)^2 \right] \right\}. \end{aligned} \quad (\text{B7})$$

#### Inhomogeneous Broadening

Write

$$\Gamma^{(N)}(E') = c_2/E^2, \quad c_2 = (\pi c)^3 \rho (\gamma_0/\gamma_D). \quad (\text{B8})$$

Let

$$I_2^{(a)}(E) = P \int_{E_{\min}}^{E_{\max}} \frac{dx}{x^2(x^2 - E^2)} = \frac{1}{E^3} \left( \frac{L}{\lambda} - \frac{\lambda}{L} \right), \quad (\text{B9})$$

leading to

$$\Delta^{(N)}(E) = \frac{2c_2 E}{\pi} I_2^{(a)}(E) = \frac{2}{\pi} \gamma_c(E) \left( \frac{L}{\lambda} - \frac{\lambda}{L} \right). \quad (\text{B10})$$

If the frequency dependence of  $\gamma_0(E')$  is included in the principal-value integrals, i. e., considering the phase-space dependence of the virtual photons renormalizing the collective eigenstates of the  $N$ -molecule system, the integrals of case (b) have to be considered.

$$\text{Case (b): } \gamma_0 = \frac{2}{3} p^2 (E'/c^3)$$

*Homogeneously Broadened Line*

Write

$$\Gamma^{(N)}(E') = c'_1 (E')^{1/2}, \quad c'_1 = \pi \left( \frac{2}{3} \rho p^2 \right)^{1/2}. \quad (\text{B11})$$

Then let

$$I_1^{(b)}(E) = P \int_{E_{\min}}^{E_{\max}} \frac{dx x^{1/2}}{x^2 - E^2} \quad (\text{B12})$$

$$= \frac{1}{E^{1/2}} \left[ \frac{\pi}{2} + \left( \frac{\lambda}{L} \right)^{1/2} - \left( \frac{D}{\lambda} \right)^{1/2} \right] \quad (\text{B13})$$

and the shift is

$$\Delta^{(N)}(E) = \frac{2E}{\pi} c'_1 I_1^{(b)}(E)$$

$$= \frac{2}{\pi} \gamma_c(E) \left[ \frac{\pi}{2} + \left( \frac{\lambda}{L} \right)^{1/2} - \left( \frac{D}{\lambda} \right)^{1/2} \right]. \quad (\text{B14})$$

Finally, this leads to the inhomogeneously broadened line.

*Inhomogeneously Broadened Line*

Write

$$\Gamma^{(N)}(E') = c'_2 E', \quad c'_2 = \frac{2}{3} p^2 (\rho \pi^3 / \gamma_D). \quad (\text{B15})$$

Take

$$I_2^{(b)}(E) = P \int_{E_{\min}}^{E_{\max}} \frac{dx x}{x^2 - E^2} \quad (\text{B16})$$

$$= \ln \frac{\lambda}{D} + \frac{1}{2} \left[ \left( \frac{\lambda}{L} \right)^2 - \left( \frac{D}{\lambda} \right)^2 \right] \quad (\text{B17})$$

and the shift is given by

$$\Delta^{(N)}(E) = \frac{2E}{\pi} c'_2 I_2^{(b)}(E) = \frac{2}{\pi} \gamma_c(E) \left\{ \ln \frac{\lambda}{D} + \frac{1}{2} \left[ \left( \frac{\lambda}{L} \right)^2 - \left( \frac{D}{\lambda} \right)^2 \right] \right\}. \quad (\text{B18})$$

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