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Evolution in time of an *N*-atom system. I. A physical basis set for the projection of the master equation

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We study an aggregate of N identical two-level atoms (TLA's) coupled by the retarded interatomic interaction, using the Lehmberg-Agarwal master equation. First, we calculate the entangled eigenstates of the system; then, we use these eigenstates as a basis set for the projection of the master equation. We demonstrate that in this basis the equations of motion for the level populations, as well as the expressions for the emission and absorption spectra, assume a simple mathematical structure and allow for a transparent physical interpretation. To illustrate the use of the general theory in emission processes, we study an isosceles triangle of atoms, and present in the long wavelength limit the (cascade) emission spectrum for a hexagon of atoms fully excited at $t=0$. To illustrate its use for absorption processes, we tabulate (in the same limit) the biexciton absorption frequencies, linewidths, and relative intensities for polygons consisting of $N=2,...,9$ TLA's.

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The coherent interaction with the radiation field of N identical two-level quantum systems has received a good deal of attention over the years. The initial impetus for the subject was an article by Dicke [1], in which he introduced the concept of ''superradiance.'' A major advance was the introduction by Lehmberg [2] and Agarwal [3] of the ''master equation,'' which has provided the foundation for most of the calculations since. Early interest in coherent excitation focused on such subjects as superradiance [4] and the theory of molecular excitons [5]. More recently, the coherent or entangled eigenstates of two-level ''qubits'' have become an active area of study in quantum information science [6], while spectroscopists have become interested in the optical properties of molecular clusters or aggregates [7], many of which properties are believed to be related to the coherent interaction of the aggregates with the radiation field.

The master equation can be solved by projection onto any complete set of basis states of the system. It is our purpose in this article to introduce as the ''natural'' set for this projection the eigenstates of the retarded interatomic interaction operator. We demonstrate that in this basis the equations of motion for the level populations, as well as the expressions for the emission and absorption spectra, assume a simple mathematical structure and allow for a particularly transparent physical interpretation.

We consider an aggregate of N identical monomers located at positions $\mathbf{R}_i$, interacting cooperatively with and via the electromagnetic field. Each monomer may be simply a single atom for example, or a quantum dot, or even a large, complicated molecule—regardless, we will focus on a single transition within the monomer between two of its (nondegenerate) energy levels $|a_i\rangle$ and $|b_i\rangle$, and refer to it simply as an atom. Our focus is on how the cooperative interaction of the atoms with the field changes the spectroscopic properties of the transition in the aggregate from those of the corresponding transition in the individual atoms.

Our starting point is the master equation, which describes the evolution in time of the system. There are two equivalent forms for this equation: One involves the reduced atomic density operator; the second, which we will use, describes the time evolution of the expectation value of an arbitrary atomic operator Q, and has the form

$$\frac{\partial\langle Q\rangle}{\partial t}=\frac{i}{\hbar}\langle[H_A,Q]\rangle+i\sum_{i,j=1}^{N}g_{ij}\langle[S_i^+S_j^-,Q]\rangle-\sum_{i,j=1}^{N}f_{ij}\langle(S_i^+S_j^-Q+QS_i^+S_j^--2S_i^+QS_j^-)\rangle, \tag{1}$$

where H_A is the atomic Hamiltonian

$$H_A=\hbar\sum_{i=1}^{N}\omega_0'S_i^+S_i^-,$$

ω_0' is the transition frequency, S_i^+ and S_i^- are the raising and lowering operators of atom i, and g_{ij} and f_{ij} are the real and imaginary parts, respectively, of the interatomic interaction Ω_{ij}. In this article, we will refer explicitly only to single-photon electric dipole transitions, for which Ω_{ij} is given by

$$\Omega_{ij}=\gamma\left[\frac{1}{2}[3(\hat{\mu}_i\cdot\hat{\mathbf{R}}_{ij})(\hat{\mu}_j\cdot\hat{\mathbf{R}}_{ij})-\hat{\mu}_i\cdot\hat{\mu}_j]h_2^{(2)}(kR_{ij})+(\hat{\mu}_i\cdot\hat{\mu}_j)h_0^{(2)}(kR_{ij})\right].$$

[3], where γ is half the Einstein A coefficient $\gamma=2|\mu|^2\omega_0'^3/3\hbar c^3$, $\vec{\mu}_i=\mu\hat{\mu}_i$ is the atomic transition moment, and $h_n^{(2)}$ is a spherical Hankel function of the second kind [8]. However, we point out that our general theory can be applied to any other type of radiative transition as well, such as magnetic dipole, electric quadrupole [9], or two-photon electric dipole [10], simply by choosing the expression for Ω_{ij} which is appropriate to the transition in question. For

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example, for linear transition quadrupoles oriented perpendicular to the plane of the ring, the interaction is

$$\Omega_{ij}=i\gamma_q\left[-\frac{9}{28}h_4^{(2)}(kr_{ij})+\frac{5}{28}h_2^{(2)}(kr_{ij})+\frac{1}{2}h_0^{(2)}(kr_{ij})\right],$$

where γ_q is half the Einstein A coefficient for the (quadrupole) transition [9]

$$\gamma_q=\frac{|q|^2\omega^5}{15\hbar c^5}.$$

Henceforth for simplicity we will suppress the expectation value brackets. We rewrite Eq. (1) in the form

$$\frac{\partial Q}{\partial t}=i\sum_{i,j=1}^{N}(\omega_0'\delta_{ij}+\Omega_{ij})S_i^+S_j^-Q-i\sum_{i,j=1}^{N}(\omega_0'\delta_{ij}+\Omega_{ij}^*)QS_i^+S_j^-+2\sum_{i,j=1}^{N}f_{ij}S_i^+QS_j^-. \tag{2}$$

It is convenient to define the operator M,

$$M\equiv\sum_{i=1}^{N}(\omega_0'+g_{ii}+if_{ii})S_i^+S_i^-+H_{int},$$

where $H_{int}=\Sigma_{i\neq j}\Omega_{ij}S_i^+S_j^-$ represents the interatomic interaction in the aggregate, an operator which exchanges the excitation between the pairs of atoms. We note that (1) g_{ii} is the atomic Lamb shift, and "renormalize" the transition frequency to include it, i.e., we set $\omega_0=\omega_0'+g_{ii}$; (2) $f_{ii}=\gamma$, the atomic self-damping constant; and (3) $\hat{n}_{op}\equiv\Sigma_{i=1}^{N}S_i^+S_i^-$ is an operator representing the number of excited atoms in the system. Thus, $M=(\omega_0+i\gamma)\hat{n}_{op}+H_{int}$, and we may rewrite Eq. (2) in the form

$$\frac{\partial Q}{\partial t}=iMQ-iQM^{\dagger}+2\sum_{i,j=1}^{N}f_{ij}S_i^+QS_j^-.$$

The master equation may be solved by projection onto any complete set of basis states. However, as demonstrated previously for the simple cases of $N=2$ and 3 [11], the natural set for this projection are the eigenstates of the (non-Hermitian) operator $H=\hbar M$: H is the effective Hamiltonian of the system of atoms "dressed" by the vacuum field [12]. The *noninteracting* Hamiltonian H_A has energy levels $n\hbar\omega_0$, which are $\binom{N}{n}$-fold degenerate. The interaction H_{int} splits this degeneracy and creates bands of eigenstates, which as we will demonstrate have the following properties.

(1) The real part of the (complex) eigenvalue gives the shift of energy of the state due to local field effects.

(2) The imaginary part of the eigenvalue gives the total decay constant (or inverse lifetime) of the state; this constant is the sum of the individual decay constants to all states in the energy manifold below.

(3) The decay rate between any pair of states agrees completely with the total energy radiated by the system in a transition between the pair.

In this article, we illustrate these properties while confining our attention for general systems to their $n=1$ and 2 manifolds. As sample applications of the general theory, we study an isosceles triangle of atoms, a fully-excited system of 6 atoms arranged on the vertices of a hexagon, and the biexciton absorption by regular polygons consisting of $N=2,...,9$ atoms. In these examples we make use of the eigenstates of a system of N atoms arranged on the vertices of a regular polygon which are calculated in an accompanying article (along with the $n=1$ or *single exciton* eigenstates for a variety of other aggregates in 2 and 3 dimensions, including "pyramid" and "diamond" structures, multiple layers, icosahedra and dodecahedra) [13].

I. GENERAL THEORY

A. Eigenstates of M

1. $n=0$: *Ground state*

The ground state of the system has all atoms in their ground states, and is denoted by $|G\rangle=\Pi_{i=1}^{N}|a_i\rangle$.

2. $n=1$: *Single excitation eigenstates*

The state of the system in which atom i is excited, while all the others remain in their ground states, is denoted by $|B_i\rangle$,

$$|B_i\rangle=|b_i\rangle\prod_{j\neq i=1}^{N}|a_j\rangle. \tag{3}$$

These are eigenstates of the noninteracting Hamiltonian H_A, but not of H, which includes the atomic interaction H_{int}. We denote the eigenstates of H by $|\alpha\rangle$,

$$|\alpha\rangle\equiv\sum_{i=1}^{N}s_i^{\alpha}|B_i\rangle.$$

These satisfy the equation

$$H|\alpha\rangle=\hbar\Omega_{\alpha}^{(1)}|\alpha\rangle=\hbar(G_{\alpha}^{(1)}+iF_{\alpha}^{(1)})|\alpha\rangle. \tag{4}$$

To find these states, we solve the eigenvalue equation of the $N\times N$ matrix representing H in the space spanned by the states $\{|B_i\rangle\}$. Because $\Omega_{ij}=\Omega_{ji}$, this matrix is symmetric, but not Hermitian. As a consequence, (1) its eigenvalues $\hbar\Omega_{\alpha}^{(1)}$ are complex; (2) its eigenvectors $\{(s_i^{\alpha})\}$ may be real or complex, depending on the system in question. In either case, they obey the orthonormality and completeness relations

$$\sum_{i=1}^{N}s_i^{\alpha}s_i^{\alpha'}=\delta_{\alpha\alpha'},\quad\sum_{\alpha=1}^{N}s_i^{\alpha}s_j^{\alpha}=\delta_{ij}. \tag{5}$$

The $n=1$ eigenstates have been calculated over the years for many atomic systems, including $N=2$ and 3 [11], linear chains [14], two-dimensional arrays [15], and circular rings and regular polygons [16]. In an accompanying article, we extend these calculations to include "pyramid" and "diamond" structures, some multiple layers, icosahedra, and dodecahedra [13].

3. $n=2$: Double excitation eigenstates

The state of the system in which atoms i and j are excited, while all the others remain in their ground states, is denoted by $|B_{ij}\rangle$,

$$|B_{ij}\rangle = |b_i\rangle |b_j\rangle \prod_{k\neq i,j}^{N} |a_k\rangle. \tag{6}$$

These are eigenstates of H_A but not of H; we denote the eigenstates of H by $|\beta\rangle$,

$$|\beta\rangle \equiv \sum_{(ij)\text{pairs}} d_{ij}^{\beta} |B_{ij}\rangle,$$

which satisfy the eigenvalue equation

$$H|\beta\rangle = \hbar\Omega_{\beta}^{(2)}|\beta\rangle = \hbar(G_{\beta}^{(2)} + iF_{\beta}^{(2)})|\beta\rangle.$$

They are found by first constructing and then diagonalizing the square matrix of dimension $N(N-1)/2$ representing H in the space spanned by the states $\{|B_{ij}\rangle\}$.

The eigenvectors $\{(d_{ij}^{\beta})\}$ obey the orthonormality and completeness relations

$$\sum_{(ij)\text{pairs}} d_{ij}^{\beta} d_{ij}^{\beta'} = \delta_{\beta\beta'}, \quad \sum_{\beta} d_{(ij)}^{\beta} d_{(ij)'}^{\beta} = \delta_{(ij)(ij)'}. \tag{7}$$

The $n=2$ eigenstates have been calculated for systems containing 2 and 3 atoms [11], and for N atoms arranged on the vertices of a regular polygon [13].

4. Eigenstates for $n>2$

The eigenstates of the system corresponding to the (simultaneous) excitation of $n>2$ atoms are calculated in an analogous manner—e.g., the $n=3$ eigenstates of $N=6$ and $N=7$ atoms arranged on the vertices of regular polygons are calculated in Ref. [13]. However, for the general theory in this article we will confine our attention (for simplicity) to systems in which no more than 2 atoms are (simultaneously) excited; this is sufficient to establish the pattern. Examples of full excitation of systems containing $N=3$ and $N=6$ atoms are presented in Secs. II A and II B.

B. Time evolution of the system

We restrict ourselves to the subspace of the system corresponding to $n\leqslant 2$. To study its evolution in time, we make use of the following table of operations:

$$M|G\rangle = 0, \quad S_i^{+}|G\rangle = \sum_{\alpha} s_i^{\alpha}|\alpha\rangle,$$

$$M|\alpha\rangle = \Omega_{\alpha}^{(1)}|\alpha\rangle, \quad S_i^{+}|\alpha\rangle = \sum_{\beta} C_i^{\alpha\beta}|\beta\rangle,$$

$$M|\beta\rangle = \Omega_{\beta}^{(2)}|\beta\rangle, \quad S_i^{+}|\beta\rangle = 0.$$

Here,

$$C_i^{\alpha\beta} = \sum_{j\neq i} s_j^{\alpha} d_{ij}^{\beta}. \tag{8}$$

It is then straightforward to show that the average values of the atomic operators $Q=\{\sigma_{GG}\equiv|G\rangle\langle G|, \sigma_{\alpha G}\equiv|\alpha\rangle\langle G|$, etc.$\}$ obey the following set of equations:

$$\dot{\sigma}_{GG} = 2\sum_{\alpha,\alpha'} T_{\alpha\alpha'}\sigma_{\alpha\alpha'},$$

$$\dot{\sigma}_{\alpha\alpha'} = [i(G_{\alpha}^{(1)} - G_{\alpha'}^{(1)}) - (F_{\alpha}^{(1)} + F_{\alpha'}^{(1)})]\sigma_{\alpha\alpha'} + 2\sum_{\beta,\beta'} N_{\beta\beta'}^{\alpha\alpha'}\sigma_{\beta\beta'},$$

$$\dot{\sigma}_{\beta\beta'} = [i(G_{\beta}^{(2)} - G_{\beta'}^{(2)}) - (F_{\beta}^{(2)} + F_{\beta'}^{(2)})]\sigma_{\beta\beta'},$$

$$\dot{\sigma}_{\beta G} = (iG_{\beta}^{(2)} - F_{\beta}^{(2)})\sigma_{\beta G},$$

$$\dot{\sigma}_{\alpha G} = (iG_{\alpha}^{(1)} - F_{\alpha}^{(1)})\sigma_{\alpha G} + 2\sum_{\beta,\alpha'} M_{\beta\alpha'}^{\alpha}\sigma_{\beta\alpha'},$$

$$\dot{\sigma}_{\beta\alpha} = [i(G_{\beta}^{(2)} - G_{\alpha}^{(1)}) - (F_{\beta}^{(2)} + F_{\alpha}^{(1)})]\sigma_{\beta\alpha},$$

where

$$T_{\alpha\alpha'} = \sum_{\mu,\nu} s_{\mu}^{\alpha} f_{\mu\nu} s_{\nu}^{*\alpha'},$$

$$N_{\beta\beta'}^{\alpha\alpha'} = \sum_{\mu,\nu} C_{\mu}^{\alpha\beta} f_{\mu\nu} C_{\nu}^{*\alpha'\beta'},$$

and

$$M_{\beta\alpha'}^{\alpha} = \sum_{\mu,\nu} C_{\mu}^{\alpha\beta} f_{\mu\nu} s_{\nu}^{*\alpha'}.$$

1. Populations

We focus first on the average populations of the levels, $\sigma_{\beta\beta}$, $\sigma_{\alpha\alpha}$ and σ_{GG}. In the secular approximation [17], these obey the equations

$$\dot{\sigma}_{\beta\beta} = -2F_{\beta}^{(2)}\sigma_{\beta\beta},$$

$$\dot{\sigma}_{\alpha\alpha} = -2F_{\alpha}^{(1)}\sigma_{\alpha\alpha} + 2\sum_{\beta} N_{\beta\beta}^{\alpha\alpha}\sigma_{\beta\beta},$$

$$\dot{\sigma}_{GG} = 2\sum_{\alpha} T_{\alpha\alpha}\sigma_{\alpha\alpha}.$$

The physical meaning of these equations is clear: The population of the ground state $|G\rangle$ increases because of the decay into it of population from the $n=1$ states $\{|\alpha\rangle\}$. Population decays *out* of $|\alpha\rangle$ at the rate $2F_{\alpha}^{(1)}\sigma_{\alpha\alpha}$, and into it from each $n=2$ level $|\beta\rangle$ above at the rate $2N_{\beta\beta}^{\alpha\alpha}\sigma_{\beta\beta}$. Because we are restricting ourselves to the states $n \leqslant 2$, there are no $n=3$ levels to decay into $|\beta\rangle$, and so population decays only out of it, at the rate $2F_\beta^{(2)}\sigma_{\beta\beta}$.

We stress that the simplicity of these equations and of their physical interpretation is due entirely to the projection of the master equation onto the eigenstates of H. The use for this projection of any other basis set—e.g., the noninteracting states of Eqs. (3) and (6)—would result in populations coupled to one another within each manifold n by the interatomic interaction. Projection onto eigenstates of this interaction results in populations uncoupled to those of other states within the same manifold, decaying independently into states in the manifold below, and with population flowing in from states in the manifold above.

Next, we evaluate the quantity $T_{\alpha\alpha'}$. If the eigenvectors $\{(s_i^\alpha)\}$ are real, the imaginary part of Eq. (4) is equivalent to the sum

$$\sum_\nu f_{\mu\nu} s_\nu^\alpha = F_\alpha^{(1)} s_\mu^\alpha .$$

Using the orthonormality of the eigenvectors we then obtain the result

$$T_{\alpha\alpha'} = F_\alpha^{(1)} \delta_{\alpha\alpha'} .$$

If the $\{(s_i^\alpha)\}$ are complex however, we cannot proceed so simply. We have verified the above relationship algebraically for the complex eigenvectors of the isosceles triangle (Sec. II A); for all other systems, we have contented ourselves with a numerical verification. Similarly, we have verified (algebraically for the triangle and numerically for other systems) that $\Sigma_\alpha N_{\beta\beta}^{\alpha\alpha} = F_\beta^{(2)}$, so that the sum of the transition rates from $|\beta\rangle$ into all states $|\alpha\rangle$ in the manifold below is equal to the total decay rate out of $|\beta\rangle$. These results are consistent with the conservation of probability, $\Sigma_i \dot\sigma_{ii} = 0$, where the sum is over all states of the system, as is required physically.

The solutions to these equations are

$$\sigma_{\beta\beta}(t) = \sigma_{\beta\beta}(0) e^{-2F_\beta^{(2)} t},$$

$$\sigma_{\alpha\alpha}(t) = \sigma_{\alpha\alpha}(0) e^{-2F_\alpha^{(1)} t} + \sum_\beta N_{\beta\beta}^{\alpha\alpha} \sigma_{\beta\beta}(0) \times \frac{e^{-2F_\beta^{(2)} t} - e^{-2F_\alpha^{(1)} t}}{F_\alpha^{(1)} - F_\beta^{(2)}},$$

$$\begin{aligned}\sigma_{GG}(t) = \sigma_{GG}(0) + \sum_\alpha \Bigg[&(1 - e^{-2F_\alpha^{(1)} t}) \Bigg\{ \sigma_{\alpha\alpha}(0) - \sum_\beta N_{\beta\beta}^{\alpha\alpha} \sigma_{\beta\beta}(0) \frac{1}{F_\alpha^{(1)} - F_\beta^{(2)}} \Bigg\} \\ &+ \sum_\beta (1 - e^{-2F_\beta^{(2)} t}) \frac{F_\alpha^{(1)}}{F_\beta^{(2)}} N_{\beta\beta}^{\alpha\alpha} \sigma_{\beta\beta}(0) \frac{1}{F_\alpha^{(1)} - F_\beta^{(2)}} \Bigg].\end{aligned}$$

2. Coherences

The dipole moment operators $\vec{\mu}_i$ are conveniently expressed in terms of the eigenstates $\{|E\rangle\}$ of the operator H,

$$\vec{\mu}_i = \sum_{E,E'} |E\rangle\langle E|\vec{\mu}_i|E'\rangle\langle E'| = \sum_{E,E'} (\vec{\mu}_i)_{EE'} \sigma_{EE'} .$$

If we again restrict ourselves to those eigenstates of H corresponding to $n \leqslant 2$, this can be rewritten in the form

$$\begin{aligned}\vec{\mu}_i &= \vec{\mu} \sum_{\alpha,\beta} (s_i^{*\alpha} \sigma_{\alpha G} + C_i^{*\alpha\beta} \sigma_{\beta\alpha}) + \text{conjugate} \\ &\equiv \vec{\mu}_i^{+}(t) + \vec{\mu}_i^{-}(t).\end{aligned}$$

Thus, there is a term in $\vec{\mu}_i$ corresponding to each of the "coherences" [17] $\sigma_{\alpha G}$ and $\sigma_{\beta\alpha}$, which represent transitions between the system eigenstates. In general, the transition frequencies are different from each other, so that in the secular approximation the coherence equations of motion can be written

$$\dot\sigma_{\beta\alpha} = [i(G_\beta^{(2)} - G_\alpha^{(1)}) - (F_\beta^{(2)} + F_\alpha^{(1)})] \sigma_{\beta\alpha} ,$$

$$\dot\sigma_{\alpha G} = (iG_\alpha^{(1)} - F_\alpha^{(1)}) \sigma_{\alpha G} ,$$

with the solutions

$$\sigma_{\beta\alpha}(t) = \sigma_{\beta\alpha}(0) e^{[i(G_\beta^{(2)} - G_\alpha^{(1)}) - (F_\beta^{(2)} + F_\alpha^{(1)})]t},$$

$$\sigma_{\alpha G}(t) = \sigma_{\alpha G}(0) e^{(iG_\alpha^{(1)} - F_\alpha^{(1)})t}.$$

Each coherence oscillates at the "Bohr" frequency of the transition to which it corresponds, and is damped at a rate equal to half the sum of the decay rates of the upper and lower eigenstates involved in the transition.

C. Emission of radiation

The electric field operator $\mathbf{E}(\mathbf{R})$ is written in terms of the creation and annihilation operators $a_{\mathbf{k}\lambda}^\dagger$ and $a_{\mathbf{k}\lambda}$,

$$\mathbf{E}(\mathbf{R}) = i\hbar \sum_{\mathbf{k},\lambda} \left(\frac{2\pi\omega}{\hbar V} \right)^{1/2} \hat{\mathbf{e}}_{\mathbf{k}\lambda} (a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}} - a_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{R}}).$$

The number of photons in the field at time t with wave vector $\mathbf{k}$ and polarization $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ is then given by

$$n(\mathbf{k}, \hat{\mathbf{e}}_{\mathbf{k}\lambda}, t) = \langle a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} \rangle_t .$$

Both the intensity and the spectrum of the emitted radiation are found to be proportional to the two-time correlation function of the atomic dipole moment operator $\langle \mu^+(t) \mu^-(t') \rangle$ [17]. The term $\langle \mu_{ij}^+(t) \mu^-(t') \rangle$ satisfies the same equation of motion for $t \geqslant t'$ as does the corresponding coherence $\langle \sigma_{ij}^+(t) \rangle$ (quantum regression theorem [18]). If we focus for example on the term corresponding to the transition from $|\alpha\rangle$ to $|G\rangle$, $P(t)$, the average power emitted at time t, is obtained (in the Markov approximation) by summing over all polarizations and directions of emission,

$$P(t)=2\pi\hbar G_\alpha^{(1)}\sigma_{\alpha\alpha}(t)\sum_{i,j} s_i^\alpha s_j^{*\alpha}\sum_{\mathbf{k},\lambda} |g_{\mathbf{k}\lambda}|^2 e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}$$

[3], while the density of emitted photons of frequency ω is

$$n(\omega)=\lim_{t\to\infty} 2\,\mathrm{Re}\sum_{i,j} s_i^\alpha s_j^{*\alpha}\sum_{\mathbf{k},\lambda} |g_{\mathbf{k}\lambda}|^2 e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)} \times\int_0^t dt_2\int_{t_2}^t dt_1 e^{-i\omega(t_1-t_2)}\sigma_{\alpha G}(t_1)\sigma_{G\alpha}(t_2), \quad (9)$$

where $g_{\mathbf{k}\lambda}=(2\pi\omega/\hbar V)^{1/2}\vec{\mu}\cdot\hat{\mathbf{e}}_{\mathbf{k}\lambda}$.

We first evaluate the sums which appear in both expressions,

$$J\equiv\sum_{i,j} s_i^\alpha s_j^{*\alpha}\sum_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}|g_{\mathbf{k}\lambda}|^2.$$

We choose our z axis in the direction of $\vec{\mu}$, and denote by α_{ij} the angle formed between $\vec{\mu}$ and $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ and by (θ,ϕ) the direction of $\mathbf{k}$. Performing first the sum over the polarizations λ, we obtain an expression for the angular distribution of the emitted radiation. We continue, replace the sum over wave vector $\mathbf{k}$ with an integral in the usual way, reintroduce the damping constant γ, and obtain for J the expression

$$J=\frac{3\gamma}{8\pi^2}\sum_{i,j} s_i^\alpha s_j^{*\alpha}\int\int e^{i\mathbf{k}\cdot\mathbf{R}_{ij}}\sin^2\theta d\Omega$$

$$=\frac{3\gamma}{8\pi^2}\int\int\left[\sum_{i=1}^N |s_i^\alpha|^2+\sum_{i\neq j} s_i^\alpha s_j^{*\alpha}\cos(\mathbf{k}\cdot\mathbf{R}_{ij})\right]\sin^2\theta d\Omega.$$

The integral over all angles of $\sin^2\theta$ is simply $8\pi/3$. To evaluate the integrals involving $\cos(\mathbf{k}\cdot\mathbf{R}_{ij})$, we first expand the cosine in the form

$$\cos(\mathbf{k}\cdot\mathbf{R}_{ij})=\cos(A\cos\theta)\cos(B\sin\theta\cos\phi) -\sin(A\cos\theta)\sin(B\sin\theta\cos\phi),$$

where $A=kR_{ij}\cos\alpha_{ij}$ and $B=kR_{ij}\sin\alpha_{ij}$. The integral over ϕ of $\sin(B\sin\theta\cos\phi)$ is 0, while from the integral representation of the Bessel function [8] the integral

$$\int_0^{2\pi}\cos(B\sin\theta\cos\phi)d\phi=2\pi J_0(B\sin\theta).$$

With the substitution $x=\cos\theta$, the integral over θ can be rewritten in the form

$$L=\int_{-1}^1\cos(Ax)J_0(B\sqrt{1-x^2})(1-x^2)dx\equiv L_1+L_2.$$

With the help of integral tables [20], L_1 is found to have the value $2\sin(kR_{ij})/kR_{ij}$. L_2 is evaluated by differentiating L_1 (twice) with respect to A, and added to L_1 to give the result

$$L=4\pi\left[(1-\cos^2\alpha_{ij})\frac{\sin(kR_{ij})}{kR_{ij}}+(1-3\cos^2\alpha_{ij})\left(\frac{\cos(kR_{ij})}{(kR_{ij})^2}-\frac{\sin(kR_{ij})}{(kR_{ij})^3}\right)\right]=\frac{8\pi}{3\gamma}f_{ij}.$$

Thus,

$$J=\frac{3\gamma}{8\pi^2}\left[\frac{8\pi}{3}\sum_{i=1}^N |s_i^\alpha|^2+\frac{8\pi}{3\gamma}\sum_{i\neq j} s_i^\alpha s_j^{*\alpha}f_{ij}\right]$$

$$=\frac{1}{\pi}\sum_{i,j} s_i^\alpha f_{ij}s_j^{*\alpha}=\frac{1}{\pi}T_{\alpha\alpha}, \quad (10)$$

and

$$P(t)=2\hbar G_\alpha^{(1)}T_{\alpha\alpha}\sigma_{\alpha\alpha}(t).$$

The average emitted power is equal to the energy of a photon at the transition frequency $G_\alpha^{(1)}$ multiplied by the rate of decay of population from $|\alpha\rangle$ into $|G\rangle$, as obtained from the master equation for the evolution in time of σ_{GG}.

With Eqs. (9) and (10), we find that $n(\omega)$, the density of photons at frequency ω emitted by an atom initially prepared in state $|\alpha\rangle$, is given by

$$n(\omega)=\frac{1}{\pi}\frac{F_\alpha^{(1)}}{(\omega-G_\alpha^{(1)})^2+(F_\alpha^{(1)})^2}:$$

a single Lorentzian line, centered at the transition frequency $G_\alpha^{(1)}$, with a width given by $2F_\alpha^{(1)}$. If the system is prepared initially in a linear combination of $n=1$ eigenstates, it is straightforward to show that the emission spectrum consists of the corresponding linear combination of Lorentzians corresponding to transitions from the constituent eigenstates to $|G\rangle$.

If the system is prepared in an $n=2$ eigenstate $|\beta\rangle$, the resulting emission is a cascade: The system decays first into states in the $n=1$ manifold, with branching ratios given by $N_{\beta\beta}^{\alpha\alpha}$ and a total decay constant of $2\Sigma_\alpha N_{\beta\beta}^{\alpha\alpha}=2F_\beta^{(2)}$. The decay processes from $|\beta\rangle$ are described by the coherences $\{\sigma_{\beta\alpha}\}$. The lines corresponding to these initial steps in the emission cascade are centered at $\{\omega=G_\beta^{(2)}-G_\alpha^{(1)}\}$, have widths $\{2(F_\beta^{(2)}+F_\alpha^{(1)})\}$, twice the sum of the decay constants of the states involved in the transition, and weights $\{N_{\beta\beta}^{\alpha\alpha}\}$. There then follow decays from each $|\alpha\rangle$ into $|G\rangle$, described by the coherences $\{\sigma_{\alpha G}\}$: lines centered at $\{G_\alpha^{(1)}\}$, with widths $\{2F_\alpha^{(1)}\}$. In an analogous way, we can describe the emission cascade resulting from an initial state which is a linear combination of $n=2$ eigenstates. Because we are dealing with eigenstates of the system, the decays in general do not interfere. (An exception can occur in unusual systems in which successive transitions happen to occur at the same frequency. In such cases, there is a "transfer of coherence" between the manifolds [17], which will affect the linewidths.)

As a simple example, in Fig. 1 we display a complete energy level diagram for an equilateral triangle of atoms

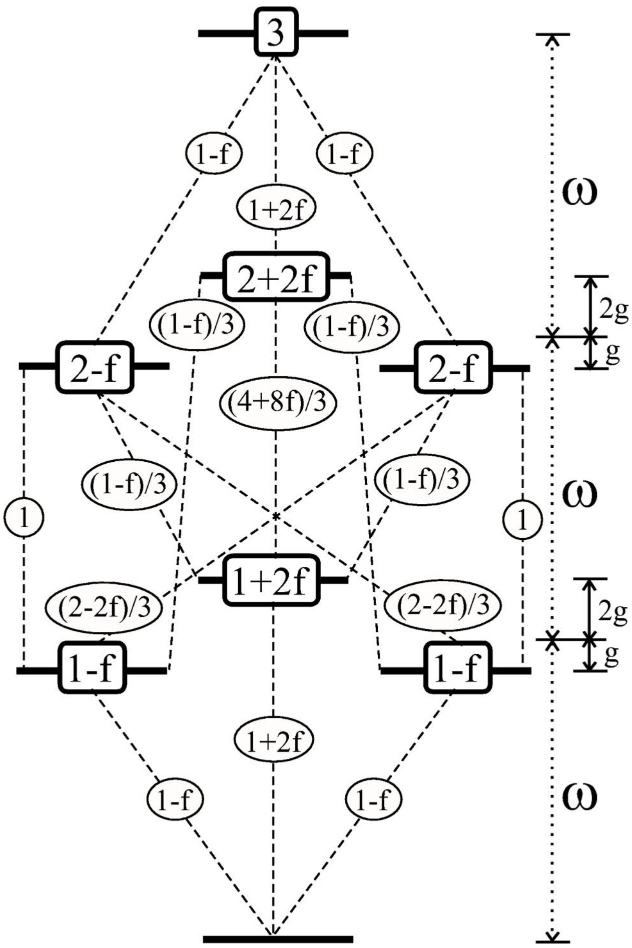

FIG. 1. Energy levels and decay rates for an equilateral triangle of atoms, in units of $\hbar$, $\gamma=1$.

[19]. All atomic separations are equal, so that the system is described by a single interaction potential $\Omega=g+if$. On each state is indicated its total decay constant, while decay constants between states are indicated on the dashed lines connecting them. For example, the $n=2$ eigenstate $(1/\sqrt{3})(1,1,1)$ has energy $\hbar 2(\omega_0+g)$ and a total decay constant of $2(\gamma+f)$; it decays with a constant of $(4\gamma+8f)/3$ to the (symmetric) $(1/\sqrt{3})(1,1,1)$ state, and $(\gamma-f)/3$ to each of the 2 antisymmetric states in the $n=1$ manifold below. Similarly, each of the other two $n=2$ eigenstates has energy $\hbar(2\omega_0-g)$ and a total decay constant of $2\gamma-f$.

It is straightforward to extend the general theory presented above to higher degrees of excitation of the system, but unnecessary: the pattern is clear. Instead, in Sec. II we illustrate the general theory using three specific examples: In Sec. II A we study in detail a system consisting of 3 atoms arranged on the vertices of an isosceles triangle; in Sec. II B, we study the emission from a fully-excited hexagon of atoms in the long-wavelength limit, $kR_{ij}\rightarrow 0$, all i and j; and in Sec. II C, we tabulate the biexciton energy levels, absorption frequencies, linewidths, and relative intensities for polygons consisting of $N=2,...,9$ atoms, in the same limit.

II. APPLICATIONS

A. Isosceles triangle

To illustrate the general theory, we present in this subsection the simple example of 3 atoms arranged on the vertices of an isosceles triangle. (In fact, the same analysis applies to a linear chain of 3 equally spaced atoms, with the middle atom labeled atom 1.) The interactions between the atoms are denoted by

$$\Omega_{12}=\Omega_{13}\equiv a=g_a+if_a, \quad \Omega_{23}\equiv b=g_b+if_b,$$

so that the matrix representing M in the $n=1$ subspace is

$$M^{(1)}=\begin{pmatrix} \omega_0+i\gamma & a & a \\ a & \omega_0+i\gamma & b \\ a & b & \omega_0+i\gamma \end{pmatrix}.$$

Its eigenvalues and associated eigenvectors are found to be

$$\Omega_1^{(1)}=\omega_0+i\gamma-b, \quad s^{(1)}=\frac{1}{\sqrt{2}}(0,-1,1), \tag{11}$$

$$\Omega_{\substack{2\\3}}^{(1)}=\omega_0+i\gamma+\frac{1}{2}(b\pm D), \quad s^{(\substack{2\\3})}=\frac{1}{N_\pm}(1,x_\pm,x_\pm), \tag{12}$$

where

$$D^2=b^2+8a^2, \quad x_\pm=(b\pm D)/4a, \quad N_\pm^2=1+2x_\pm^2. \tag{13}$$

Choosing the basis states in the order $\{|B_{12}\rangle,|B_{23}\rangle,|B_{31}\rangle\}$, we write the matrix representing M in the $n=2$ subspace in the form

$$M^{(2)}=\begin{pmatrix} 2(\omega_0+i\gamma) & a & b \\ a & 2(\omega_0+i\gamma) & a \\ b & a & 2(\omega_0+i\gamma) \end{pmatrix}.$$

Its eigenvalues and associated eigenvectors are then found to be

$$\Omega_1^{(2)}=2(\omega_0+i\gamma)-b, \quad d^{(1)}=\frac{1}{\sqrt{2}}(-1,0,1), \tag{14}$$

$$\Omega_{\substack{2\\3}}^{(2)}=2(\omega_0+i\gamma)+\frac{1}{2}(b\pm D), \quad d^{(\substack{2\\3})}=\frac{1}{N_\pm}(x_\pm,1,x_\pm). \tag{15}$$

It is easily verified that the eigenvectors satisfy the orthonormality and completeness relations (5) and (7).

We now consider the evolution in time of the system, as determined using the master equation. In the secular approximation, the level populations obey the equations

$$\dot{\sigma}_{EE}=-6\gamma\sigma_{EE},$$

$$\dot{\sigma}_{\beta\beta} = -2F_{\beta}^{(2)}\sigma_{\beta\beta} + 2T_{EE}^{\beta\beta}\sigma_{EE},$$

$$\dot{\sigma}_{\alpha\alpha} = -2F_{\alpha}^{(1)}\sigma_{\alpha\alpha} + 2\sum_{\beta} N_{\beta\beta}^{\alpha\alpha}\sigma_{\beta\beta},$$

$$\dot{\sigma}_{GG} = 2\sum_{\alpha} \sigma_{\alpha\alpha}T_{\alpha\alpha},$$

where

$$T_{EE}^{\beta\beta} = \sum_{\substack{\mu\neq(ij)\\ \nu\neq(ij)'}} d_{(ij)}^{\beta} f_{\mu\nu} d_{(ij)'}^{*\beta}.$$

For the conservation of probability, we require the following three identities to hold:

$$(1)\quad T_{\alpha\alpha} = F_{\alpha}^{(1)},$$

$$(2)\quad \sum_{\alpha} N_{\beta\beta}^{\alpha\alpha} = F_{\beta}^{(2)},$$

$$(3)\quad \sum_{\beta} T_{EE}^{\beta\beta} = F_E = 3\gamma.$$

(1) The rate of decay of population out of $|\alpha\rangle$ is given by $2F_{\alpha}^{(1)}\sigma_{\alpha\alpha}$, while the associated emission of energy and flow of population into $|G\rangle$ is given by $2T_{\alpha\alpha}\sigma_{\alpha\alpha}$. It is trivial to demonstrate that $T_{11} = F_1^{(1)} = \gamma - f_b$; instead, we calculate T_{22},

$$T_{22} = \frac{1}{|N_+|^2}(1 \quad x_+^* \quad x_+^*)\begin{pmatrix} \gamma & f_a & f_a \\ f_a & \gamma & f_b \\ f_a & f_b & \gamma \end{pmatrix}\begin{pmatrix} 1 \\ x_+ \\ x_+ \end{pmatrix}$$

$$= \frac{1}{|N_+|^2}[(1+2|x_+^2|)\gamma + 2f_b|x_+^2| + 4f_a \operatorname{Re} x_+].$$

By substitution into the eigenvalue equation for $M^{(1)}$, we find that the quantity $(b+D)/2$ can be written in two ways:

$$\frac{b+D}{2} = 2ax_+ = b + \frac{a}{x_+}. \tag{16}$$

Writing $x_+ = |x_+|e^{i\phi}$, we rewrite Eq. (16) in the form

$$\begin{aligned}\operatorname{Im}((b+D)/2) &= \operatorname{Im}(2ax_+)\\ &= 2|x_+|(f_a\cos\phi + g_a\sin\phi)\\ &= \operatorname{Im}\left(b + \frac{a}{x_+}\right)\\ &= f_b + (1/|x_+|)(f_a\cos\phi - g_a\sin\phi).\end{aligned}$$

We multiply the second of these equations by $2|x_+^2|$ and add it to the first to obtain

$$(1+2|x_+^2|)\operatorname{Im}((b+D)/2) = 2f_b|x_+^2| + 4f_a\operatorname{Re} x_+.$$

Dividing by $|N_+|^2$ and comparing with Eq. (12), we find that

$$T_{22} = \frac{1+2|x_+|^2}{|1+2x_+^2|}F_2^{(1)}.$$

It is easy to verify that the factor $(1+2|x_+|^2)/|1+2x_+^2|$ in the above expression differs from 1 by an amount of order $\operatorname{Im}(b+D)/\operatorname{Re}(b+D)$, an error which was introduced by our having made the secular approximation. Because f_a, $f_b \leqslant \gamma$, while g_a, $g_b \simeq (kR)^{-3}\gamma$, this difference in practice is $\leqslant 10^{-6}$, and therefore negligible, so that $T_{22} = F_2^{(1)}$ (within the accuracy of the secular approximation). The equivalent relation for T_{33} is obtained in an identical way. Thus we have demonstrated directly that the decay of population out of each $n=1$ eigenstate is equal to the rate at which it flows into the ground state $|G\rangle$, which in turn agrees (exactly) with the rate at which energy is radiated by a system prepared in the eigenstate (Sec. I C).

(2) Here we must verify that $\Sigma_{\alpha}N_{\beta\beta}^{\alpha\alpha}$, the sum of the decay constants of the population from each $n=2$ state $|\beta\rangle$ into the $n=1$ states $\{|\alpha\rangle\}$ below, is equal to the total decay constant of $|\beta\rangle$, as given by the imaginary part of its energy eigenvalue $F_{\beta}^{(2)}$. This is a straightforward but tedious calculation, and we will content ourselves with its demonstration for $\beta=1$ only.

We begin by calculating the vectors $\{C^{\alpha 1}\}$. Using Eqs. (8), (11), (14), and (15), we obtain the results

$$C^{11} = (1,0,0), \quad C^{21} = \frac{1}{\sqrt{2}N_+}(0,-1,1),$$

$$C^{31} = \frac{1}{\sqrt{2}N_-}(0,-1,1).$$

Proceeding with the multiplication of these vectors with the matrix $(f_{\mu\nu})$ as in the calculation of T_{22} above, we find that

$$N_{11}^{11} = \gamma, \quad N_{11}^{22} = \frac{1}{|N_+|^2}(\gamma - f_b), \quad N_{11}^{33} = \frac{1}{|N_-|^2}(\gamma - f_b),$$

whose sum is $\gamma + (\gamma - f_b)(1/|N_+|^2 + 1/|N_-|^2)$. Substituting for $|N_{\pm}|^2$ from Eq. (13), we find that $(1/|N_+|^2 + 1/|N_-|^2) = 1 +$ terms of order $[\operatorname{Im}(b+D)/\operatorname{Re}(b+D)]$, so that within the secular approximation

$$\sum_{\alpha} N_{11}^{\alpha\alpha} = 2\gamma - f_b = F_1^{(2)},$$

as required. The corresponding relations for $\beta=2$ and 3 are verified in an equivalent way.

(3) It is simple to demonstrate that because of the symmetry of the system $T_{EE}^{ii} = T_{ii} = F_i^{(1)}$ for $i = 1,\ldots,3$, so that

$$\sum_{\beta} T_{EE}^{\beta\beta} = \sum_{\beta} F_{\beta}^{(1)} = 3\gamma,$$

as required.

Thus, we have demonstrated the validity of all 3 identities, and therefore too the conservation of probability in the system.

If the system is fully excited at $t=0$, i.e. $\sigma_{EE}(0)=1$, the solutions of the population equations can be written in the form

$$\sigma_{EE}(t)=e^{-6\gamma t},$$

$$\sigma_{\beta\beta}(t)=\frac{T_{EE}^{\beta\beta}}{3\gamma-F_{\beta}^{(2)}}\left(e^{-2F_{\beta}^{(2)}t}-e^{-6\gamma t}\right),$$

$$\sigma_{\alpha\alpha}(t)=\sum_{\beta}\frac{N_{\beta\beta}^{\alpha\alpha}T_{EE}^{\beta\beta}}{3\gamma-F_{\beta}^{(2)}}\left[\frac{1}{F_{\beta}^{(2)}-F_{\alpha}^{(1)}}\left(e^{-2F_{\alpha}^{(1)}t}-e^{-2F_{\beta}^{(2)}t}\right)-\frac{1}{3\gamma-F_{\alpha}^{(1)}}\left(e^{-2F_{\alpha}^{(1)}t}-e^{-6\gamma t}\right)\right],$$

$$\sigma_{GG}(t)=\sum_{\alpha,\beta}\frac{F_{\alpha}^{(1)}N_{\beta\beta}^{\alpha\alpha}T_{EE}^{\beta\beta}}{3\gamma-F_{\beta}^{(2)}}\left[\frac{1}{F_{\beta}^{(2)}-F_{\alpha}^{(1)}}\left(\frac{1-e^{-2F_{\alpha}^{(1)}t}}{F_{\alpha}^{(1)}}-\frac{1-e^{-2F_{\beta}^{(2)}t}}{F_{\beta}^{(2)}}\right)-\frac{1}{3\gamma-F_{\alpha}^{(1)}}\left(\frac{1-e^{-2F_{\alpha}^{(1)}t}}{F_{\alpha}^{(1)}}-\frac{1-e^{-6\gamma t}}{3\gamma}\right)\right].$$

To calculate the spectrum of the radiation emitted in this cascade to the ground state, we proceed as in the general theory: We calculate the dipole moment operator $\vec{\mu}$, solve the equations of motion for each of the coherences $\{\sigma_{E\beta},\sigma_{\beta\alpha},\sigma_{\alpha G}\}$ which appear in $\vec{\mu}$ and for the two-time correlation function $\langle\mu^{+}(t)\mu_{-}(t')\rangle$, and finally calculate $n(\omega)$, for which we obtain the expression

$$n(\omega)=\sum_{\alpha,\beta}\left[\frac{T_{EE}^{\beta\beta}}{F_E}\left\{L(E,\beta)+\frac{N_{\beta\beta}^{\alpha\alpha}}{F_{\beta}^{(2)}}\left[L(\beta,\alpha)+L(\alpha,G)\right]\right\}\right],$$

where $L(X,Y)$ is the Lorentzian function of area 1 corresponding to the transition from level $|X\rangle$ to level $|Y\rangle$,

$$L(X,Y)=\frac{1}{\pi}\frac{F_X+F_Y}{(\omega-G_X+G_Y)^2+(F_X+F_Y)^2}.$$

The physical interpretation of this expression is clear.

(1) The system begins in state $|E\rangle$ which has an energy corresponding to that of 3 photons, $3\hbar\omega_0$. It then emits its first photon: Because the emission is a coherent process involving all 3 atoms, the decay occurs (on average) into the 3 $n=2$ coherently excited states $\{|\beta\rangle\}$, with a branching ratio of $T_{EE}^{\beta\beta}/F_E$ equal to the decay rate $T_{EE}^{\beta\beta}$ from $|E\rangle$ to $|\beta\rangle$ divided by the total decay rate F_E from $|E\rangle$. The sum of these branching ratios is (of course) 1, and each emission line is the Lorentzian $L(E,\beta)$, centered at the transition frequency $G_E-G_{\beta}^{(2)}$, with width $2(F_E+F_{\beta}^{(2)})$.

(2) From each state $|\beta\rangle$, the system decays coherently into the $n=1$ states $\{|\alpha\rangle\}$, with (a second) branching ratio of $N_{\beta\beta}^{\alpha\alpha}/F_{\beta}^{(2)}$, the decay rate from $|\beta\rangle$ to $|\alpha\rangle$ divided by the total decay rate from $|\beta\rangle$. There are 9 Lorentzian lines corresponding to the emission of this (second) photon, 1 line for each $|\beta\rangle\rightarrow|\alpha\rangle$ transition, with a total area of 1.

(3) From each state $|\alpha\rangle$, the system decays into the ground state $|G\rangle$, emitting a Lorentzian line $L(\alpha,G)$. The weight $W(\alpha)$ of the line beginning from $|\alpha\rangle$ corresponds to the fraction of the population which has arrived in $|\alpha\rangle$ via its various routes, $W(\alpha)=\Sigma_{\beta}(T_{EE}^{\beta\beta}/F_E)\times(N_{\beta\beta}^{\alpha\alpha}/F_{\beta}^{(2)})$, and the total area of the lines $\Sigma_{\alpha}W(\alpha)L(\alpha,G)$ is 1.

There is a well-known classical model which can be used to describe cooperative transitions of a system of N atoms between its ground and single exciton states, which helps illuminate the physics of the process. In it, atom i is replaced by an oscillating electric dipole $\vec{\mu}_i$ at the position $\mathbf{R}_i$. Dipole i creates an electric field $\mathbf{E}_i(\mathbf{R}_j)$ at the position of (every other) dipole j, which can be divided into two parts: One part is in phase with the displacement $\vec{\mu}_j$ oscillator j, and thus changes its effective frequency. The second is in phase with its velocity $\dot{\vec{\mu}}_j$, and alters its rate of damping.

We first calculate the normal modes of oscillation of the system, a step equivalent to the quantum-mechanical calculation of the (single) exciton eigenstates. The normal mode eigenvalues are complex: The real part gives the effective frequency of oscillation of each dipole in the (local) field created by all the others, and the imaginary part its net rate of damping, under the influence of its own force of radiative reaction plus that exerted on it by all the others. In a normal mode, the relative amplitudes and phases of oscillation of the dipoles adjust themselves so that the effective frequencies and dampings of all are equal; hence, no dephasing occurs during the oscillation. The eigenvectors, which are also complex, give these relative amplitudes and phases: The radiative properties of the system in a transition between $|\alpha\rangle$ and $|G\rangle$ are the same as those of a set of classical oscillating dipoles of moment $\vec{\mu}_i=\vec{\mu}\langle\alpha|S_i^{+}|G\rangle=\vec{\mu}s_i^{\alpha}$ at the positions $\mathbf{R}_i$ of the atoms. The ratio of the absolute values of the coefficients $|s_i^{\alpha}/s_j^{\alpha}|$ gives their relative amplitude; if we write $s_i^{\alpha}\equiv|s_i^{\alpha}|e^{i\phi_i}$, then their relative phase is $\phi_i-\phi_j$.

The dynamics of the system are best described in terms of these normal modes, which evolve independently of each other. Unlike the master equation calculation, which produces a balance correct only to within the accuracy of the secular approximation, here we find that the energy radiated by the atomic system into the field is *exactly* balanced by the decay of the energy of oscillation due to the damping [21]. The total work performed by the oscillators against the net damping force acting on each gives the same result. If the system is set oscillating in one of its normal modes, the total intensity of emission decays exponentially at a rate given by the imaginary part of the eigenvalue, and the spectrum of the emitted radiation consists of a single Lorentzian line, centered at the effective frequency and with a width equal to the damping rate of the mode. If the initial state is a linear combination of modes, the intensity of emission is a linear combination of exponentials and the emission spectrum the equivalent linear combination of Lorentzians corresponding to the constituent modes.

There is no existing classical model by which one can calculate the $n=2$ (or higher) eigenstates of the atomic system. In that connection however it is interesting to note that the radiative properties of the system in a transition between an $n=2$ eigenstate $|\beta\rangle$ and an $n=1$ eigenstate $|\alpha\rangle$ are identical with those of a set of classical dipoles of moment $\vec{\mu}_i = \vec{\mu}\langle\beta|S_i^+|\alpha\rangle = \vec{\mu}C_i^{\alpha\beta}$ located at the atomic positions $\mathbf{R}_i$; and so on for transitions among eigenstates corresponding to higher values of n.

B. Hexagon

In Ref. [13], we calculate the complete set of eigenstates for a system of atoms arranged at the vertices of a hexagon of arbitrary size relative to the radiation wavelength. If the system is prepared in the fully-excited state $|E\rangle$, it will emit radiation and cascade down its energy-level ladder to the ground state $|G\rangle$. As the number of states in the manifold corresponding to n excited atoms is $\binom{6}{n}$, in general this gives rise to a very large number of emission lines: $\Sigma_{n=0}^{5}\binom{6}{6-n}\binom{6}{5-n}$. In the long-wavelength limit however, the emission (like the absorption) is confined to the subspace of totally symmetric eigenstates; for the hexagon, there remain 26 spectral lines in the cascade. Their calculation is a straightforward extension to $N=n=6$ of the general theory described in this paper. We use the eigenstates of [13] in the long-wavelength limit to calculate the shifts, widths, and weights of these cascade emission lines.

For long wavelengths, there is only one optically active $n=1$ state $|\alpha\rangle$, namely that corresponding to $s_i^{(\alpha)} = 1/\sqrt{6}$. (Similarly, the only optically active state in the $n=5$ subspace is $|\epsilon\rangle = (1/\sqrt{6})\Sigma_{i=1}^{6}|A_i\rangle$, where $|A_i\rangle = |a_i\rangle\Pi_{j\neq i=1}^{6}|b_j\rangle$.) For $n=2$ (and by symmetry $n=4$), it can be shown that the active states are described by vectors of the form

$$|\beta_i\rangle = \frac{1}{\sqrt{M_{rs}}}(1,...,1;r,\ldots,r;s,s,s)$$

(in the basis $\{|B_{12}\rangle,\ldots,|B_{61}\rangle;|B_{13}\rangle,\ldots,|B_{62}\rangle;|B_{14}\rangle,|B_{25}\rangle,|B_{36}\rangle\}$), where r and s take the values

$$r_1 = 1.417 - 1.261i/V_6,\quad s_1 = 1.548 - 1.732i/V_6,$$

$$r_2 = -0.114 - 0.373i/V_6,\quad s_2 = -1.087 - 0.550i/V_6,$$

$$r_3 = -1.940 - 0.312i/V_6,\quad s_3 = 2.252 + 0.200i/V_6,$$

$\hbar V_6\gamma$ is the nearest-neighbor interaction energy in the hexagon, and the normalization constant $M_{rs} = 6 + 6r^2 + 3s^2$. For $n=3$, the active states are of the form

$$|\gamma_i\rangle = \frac{1}{\sqrt{M_{xy}}}(1,...,1;x,\ldots,x;x,\ldots,x;y,y)$$

(in the basis $\{|B_{123}\rangle,\ldots,|B_{612}\rangle;|B_{124}\rangle,\ldots,|B_{613}\rangle;|B_{134}\rangle,\ldots,|B_{623}\rangle;|B_{135}\rangle,|B_{246}\rangle\}$), where x and y take the values

$$x_1 = 1.5277 - 1.5355i/V_6,\quad y_1 = 2.0144 - 3.0116i/V_6,$$

$$x_2 = -0.05194 - 0.3278i/V_6,\quad y_2 = -1.2530 - 0.6190i/V_6,$$

$$x_3 = -0.9028 - 0.07839i/V_6,\quad y_3 = 2.6189 + 0.1431i/V_6,$$

and the normalization constant $M_{xy} = 6 + 12x^2 + 2y^2$. It is then straightforward to show that the transition probability from $|\alpha\rangle$ to $|G\rangle$ (and from $|E\rangle$ to $|\epsilon\rangle$) is 6γ, while those from $|\beta_i\rangle$ to $|\alpha\rangle$ are given by the expression

$$N_{\beta_i,\alpha} = 6\gamma\frac{|2+2r+s|^2}{|M_{rs}|},$$

and those from $|\gamma_j\rangle$ to $|\beta_i\rangle$ by

$$T_{\gamma_j\beta_i} = 36\gamma\frac{|2+2x+r(1+2x+y)+2sx|^2}{|M_{xy}||M_{rs}|}.$$

We list the frequency shifts $G_X - G_Y - \omega_0$, half-widths $F_X + F_Y$, and weights $P_X(F_{XY}/F_X)$ of the cascade emission lines from a fully-excited hexagon in Table I. Here, X and Y refer to the upper and lower states involved in the transition,

TABLE I. Cascade emission lines from a fully-excited hexagon, long-λ limit.

Transition		Shift	Half-width	
n_X	n_Y	(units of $V_6\gamma$)	(units of γ)	Weight
6	5	−2.511	16	1
5	4	−1.651	21.687	0.9687
		2.801	12.293	0.0293
		5.611	12.020	0.0020
4	3	−0.5747	23.235	0.9492
		4.2126	14.136	0.0195
		6.0871	13.689	$<10^{-4}$
		−5.0267	13.841	0.0012
		−0.2394	4.742	0.0219
		1.6351	4.295	0.0062
		−7.8367	13.568	$<10^{-4}$
		−3.0494	4.469	0.0005
		−1.1749	4.022	0.0015
3	2	0.5747	21.235	0.9424
		5.0267	11.841	0.0080
		7.8367	11.568	$<10^{-4}$
		−4.2126	12.136	0.0040
		0.2394	2.742	0.0294
		3.0494	2.469	0.0085
		−6.0871	11.689	$<10^{-4}$
		−1.6351	2.295	0.0019
		1.1749	2.022	0.0058
2	1	1.651	15.687	0.9464
		−2.801	6.293	0.0393
		−5.611	6.020	0.0143
1	0	2.511	6	1

TABLE II. $n=1$ frequency shifts in the long-wavelength limit (units of $V\gamma$).

N	v	Frequency shift	Nearest neighbors only	Linear dipoles, all neighbors	Linear quadrupoles, all neighbors
5	1, 4	$0.618a-1.618b$	0.618	0.239	0.474
	2, 3	$-1.618a+0.618b$	-1.618	-1.473	-1.563
	5	$2a+2b$	2	2.468	2.178
6	1, 5	$a-b-c$	1	0.683	0.905
	2, 4	$-a-b+c$	-1	-1.067	-1.033
	3	$-2a+2b-c$	-2	-1.741	-1.902
	6	$2a+2b+c$	2	2.509	2.159

P_X is the population passing through state $|X\rangle$ during the cascade process, and F_{XY}/F_X is the branching ratio from $|X\rangle$ to $|Y\rangle$.

C. Absorption by regular polygon systems

There exist in biology molecular aggregates known as ‘‘light-harvesting complexes,’’ in which large identical building blocks or monomers are arranged symmetrically in rings with an N-fold symmetry axis, whose electronic excitations have been found to extend coherently over the entire ring [22]. A calculation of the $n=1$ and $n=2$ eigenstates of regular polygon systems of odd N for electric dipole interactions in the long-wavelength limit has in fact been carried out [7], but in that reference the authors included only nearest-neighbor coupling for the real part of the interaction. For the $n=1$ subspace, the resulting eigenstates are the same as ours (which however include interactions between *all* neighbors and are valid for arbitrary wavelength), but the energies are very different: This difference is illustrated in Table II, where we list the $n=1$ frequency shifts in the long-wavelength limit for polygons having $N=5$ and $N=6$ for nearest-neighbor interactions only, for linear dipoles with all neighbors included, and for linear quadrupoles with all neighbors included. (All shifts are expressed in units of the static interaction energy $V\gamma$ between a pair of nearest neighbors.) For the $n=2$ subspace, the eigenstates themselves are very different from those obtained when only nearest-neighbor interactions are included, and a numerical comparison of the energies is not meaningful. Because the retarded interactions are intrinsically long-ranged, a correct calculation of the eigenstates of the physical system *must* include interactions between all atom pairs: Only in these states will the ‘‘local field’’ shifts be the same, and only in these states will the

TABLE III. Frequency shifts and widths of the exciton and biexciton energy levels (long-wavelength limit); shifts are in units of $V\gamma$, widths in units of γ.

N	$\Delta G^{(1)}_{(N)}$	$n=2$ eigenvectors	$\Delta G^{(2)}_{(vi)}$	$F^{(2)}_{(vi)}$
2	1	(1)	0	2
3	2	(1,1,1)	2	4
4	2.354	$(1,1,1,1;\ x,x)$		
		$x=1.248-0.283i/V$	3.204	5.930
		$x=-1.602-0.363i/V$	-2.496	0.070
5	2.472	$(1,1,1,1,1;\ x,x,x,x,x)$		
		$x=1.356+0.649i/V$	3.823	7.821
		$x=-0.737-0.352i/V$	-1.351	0.179
6	2.511	$(1,1,1,1,1,1;\ x,x,x,x,x,x;\ y,y,y)$		
		$x=1.417-1.261i/V;\ y=1.548-1.732i/V$	4.162	9.687
		$x=-0.114-0.373i/V;\ y=-1.087-0.550i/V$	-0.290	0.293
		$x=-1.940-0.312i/V;\ y=2.252+0.200i/V$	-3.100	0.020
7	2.518	$(1,1,1,1,1,1,1;\ x,x,x,x,x,x,x;\ y,y,y,y,y,y,y)$		
		$x=1.45-1.602i/V;\ y=1.66-2.738i/V$	4.358	11.534
		$x=0.314-0.433i/V;\ y=-0.877-0.765i/V$	0.570	0.410
		$x=-1.416-0.379i/V;\ y=0.634+0.011i/V$	-2.410	0.056
8	2.515	$(x,x,x,x,x,x,x,x;\ 1,1,1,1,1,1,1,1;\ y,y,y,y,y,y,y,y;\ z,z,z,z)$		
		$x=0+59.68i/V;\ y=1.177-0.949i/V;\ z=1.237-1.444i/V$	4.478	13.37
		$x=1.635+69.72i/V;\ y=0-0.0714i/V;\ z=-1.809-132.87i/V$	1.248	0.528
		$x=-1.0914-285.ii/V;\ y=0.4523+0.0204i/V;\ z=-1.284+0.453i/V$	-1.60	0.097
		$x=-0.490-63.44i/V;\ y=-1.33-43.48i/V;\ z=1.451-34.91i/V$	-3.322	0.008
9	2.508	$(1,...,1;\ x,\ldots,x;\ y,\ldots,y;\ z,\ldots,z)$		
		$x=1.493-2.834i/V;\ y=1.793-5.665i/V;\ z=1.939-7.341i/V$	4.559	15.19
		$x=0.822-0.583i/V;\ y=-0.144-1.184i/V;\ z=-1.015-1.518i/V$	1.780	0.644
		$x=-0.496-0.429i/V;\ y=-0.916-0.396i/V;\ z=0.713-0.0443i/V$	0.958	0.140
		$x=-1.713-0.386i/V;\ y=1.538+0.177i/V;\ z=-0.619-0.22i/V$	-2.874	0.025

TABLE IV. Biexciton excitation frequency shifts, natural linewidths, and relative intensities (long-wavelength limit).

N	Frequency shifts (units of $V\gamma$)	Half-widths (units of γ)	Relative intensities
2	-1	4	1
3	0	7	1
4	0.85	9.93	0.988
	-4.85	4.07	0.012
5	1.351	12.821	0.978
	-3.823	5.179	0.022
6	1.651	15.687	0.969
	-2.801	6.293	0.029
	-5.611	6.020	0.002
7	1.840	18.534	0.961
	-1.948	7.410	0.034
	-4.929	7.056	0.005
8	1.964	21.370	0.9550
	-1.266	8.528	0.0377
	-4.174	8.097	0.0069
	-5.836	8.008	0.0006
9	2.052	24.190	0.9494
	-0.727	9.644	0.0403
	-3.465	9.410	0.0088
	-5.381	9.025	0.0016

damping be the same for all atoms, so that no dephasing occurs during the evolution in time [23]. As well, in some systems the energy of interaction between second (or higher) nearest neighbors can actually *exceed* that between adjacent pairs (depending on the relative phases of the moments in the given eigenstate, and/or on the relative orientations of the transition moments and $\mathbf{R}_{ij}$).

If a system in its ground state is placed in a weak external field of wave vector $\mathbf{k}$ and polarization $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$, only the $n=1$ states are excited, with a relative probability proportional to $|\langle u_{(v)}|\Sigma_i S_i^+ \vec{\mu}\cdot\hat{\mathbf{e}}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}_i}|G\rangle|^2$. If the field is sufficiently intense and the losses sufficiently low, population can remain in the $\{u_{(v)}\}$ states for long enough to allow excitation of the $n=2$ states; and so on.

In recent years, there has been interest in the excitation of the exciton and biexciton states of the light-harvesting complexes, in connection with the calculation of their third-order nonlinear optical susceptibilities [7,22]. The complexes discovered so far have diameters of the order of 10 nm and their absorption frequencies correspond typically to wavelengths $\geqslant 400$ nm, so that the long-wavelength limit applies. In this limit, the dependence on $\mathbf{k}$ in the absorption probability is negligible, and it is easy to verify that only those states $\{u_{(v)}\}$ which are totally symmetric in the atomic positions are optically active, namely the states $u_{(N)} = (1/\sqrt{N})(1,...,1)$. This gives rise to Lorentzian (exciton) absorption lines, centered at the shifted frequencies $G^{(1)}_{(N)} \equiv \omega_0 + \Delta G^{(1)}_{(N)}$, with (natural) widths $2F^{(1)}_{(N)} = 2N_{\gamma}$.

We denote the frequency of state $U_{(vi)}$ by $G^{(2)}_{(vi)} = 2\omega_0 + \Delta G^{(2)}_{(vi)}$, and its decay constant by $F^{(2)}_{(vi)}$. The excitation of state $U_{(vi)}$ from a ring in the state $u_{(N)}$ then occurs at frequency $G^{(2)}_{(vi)} - G^{(1)}_{(N)}$. Like the corresponding emission line, the width of the absorption line is $2(F^{(2)}_{(vi)} + F^{(1)}_{(N)})$, and in the long-wavelength limit the relative intensities of the biexciton absorption lines are simply given by $F^{(2)}_{(vi)}$.

In Table III we list the $n=1$ shifts $\Delta G^{(1)}_{(N)}$, the (unnormalized) $n=2$ eigenvectors $\{U_{(vi)}\}$, and the $n=2$ shifts $\Delta G^{(2)}_{(vi)}$ and decay constants $F^{(2)}_{(vi)}$ for $N=2,...,9$ in the long-wavelength limit, obtained from the general solutions of Ref. [13]. The vectors $\{U_{(vi)}\}$ correspond to basis states arranged in the order $\{|B_{12}\rangle, |B_{23}\rangle, \ldots, |B_{N1}\rangle; |B_{13}\rangle, |B_{24}\rangle, \ldots, |B_{N2}\rangle;$ etc.$\}$. In Table IV we list the corresponding biexciton frequency shifts, (natural) half widths, and relative intensities. All frequencies are expressed in units of $V\gamma$, and widths in units of γ.

III. CONCLUSIONS

The evolution in time and the spectroscopic properties of an aggregate of N identical two-level atoms interacting with and via the radiation field are most easily studied using the Lehmberg-Agarwal master equation. This equation can be solved by projection onto any complete set of basis states of the system. We have demonstrated that the "natural" basis set for this projection is the set of eigenstates of the retarded interatomic interaction operator: In this basis, the equations of motion for the level populations, as well as the expressions for the absorption and emission spectra, assume a simple mathematical structure and allow for a particularly transparent physical interpretation.

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