Optical coherence properties of collective molecular systems: A comparison of the statistical and quantum approaches

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Optical coherence properties of collective molecular systems: A comparison of the statistical and quantum approaches[a)]

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The formalism of collective (Dicke-like) states and operators is used to describe the relaxation of the initially prepared state of a material in the presence of a laser field. The material states are shown to be expressible as minimum uncertainty wave packets formed from those special collective states that couple with the radiation field. It is shown that these coherent states of matter exhibit all the features that are usually attributed to ensemble averages of two-level molecules in a conventional statistical picture. However, there are new features in the quantum mechanical model when there are correlations among the molecules in the ensemble. The loss of minimum uncertainty characteristics of the wave packet correspnds to the transverse (T_2) relaxation of the statistical model. Different types of T_2 processes can be defined corresponding to the decay of different orders of coherence of the wave packet. Only for the case that the system decays in all orders of coherence do the quantum and statistical results coincide. There is expected to be a transverse relaxation that preserves one or more orders of coherence. Experiments are suggested that can test these ideas. A particular case of the formalism of collective states applies to molecular crystals and it provides a quantum mechanical picture of the dephasing of molecular excitons in terms of orders of coherence analogous to the usual manner of describing states of the radiation field.

I. INTRODUCTION

Coherent optical effects are being used more and more to study novel aspects of molecular spectroscopy and chemical dynamics. This new field is heavily indebted to the language and principles developed for magnetic resonance spectroscopy.[1] Examples of laser experiments that were designed as direct analogs of NMR situations are photon echoes, optical nutation, and optical free induction decay, and there are many others.[2] The geometrical concepts developed for NMR have been generalized by Feynman, Vernon, and Hellwarth[3] to the description of optically excited coherent states in collections of molecules. The collection is regarded as a statistical ensemble of two-level molecules, while the coherent state is understood as a statistical state of the ensemble describable through a two-dimensional density matrix in which each two-level molecule in the ensemble is excited into a superposition of its ground and excited states. Coherence is lost when a static frequency distribution or dynamic stochastic processes cause a phase randomization among the constituents of the ensemble, resulting in a decay of the macroscopic polarization.

Theories based on the description of radiative emission in terms of the macroscopic polarization of the radiating medium fail to account for effects such as spontaneous emission[4] or the spontaneous initiation of processes like stimulated Raman,[5] so that a noise field arising from vacuum fluctuations is usually postulated. The inadequacy of the conventional statistical model is

also apparent in the treatment of coherent states in molecular crystals. Such systems are *not* equivalent to statistical ensembles of two-level molecules, and their optical properties cannot be properly described by the ensemble average of the corresponding molecular properties. Instead, the intramolecular excitations in crystals must be viewed as extended quantum mechanical states—Frenkel excitons. An additional difficulty arises in the description of the coherence-loss process in low temperature crystals. In such systems there are no sudden and random processes analogous to collisions so that coherence loss cannot be treated by conventional Bloch-like equations.

In order to account for the spontaneous character of quantum transitions occurring in optically excited coherent states, for the cooperative behavior of molecules as is encountered in coherent excitations in crystals, and for the coherence loss process in the absence of time-dependent stochastic fluctuations, a completely quantum mechanical description for the coherent states of a collection of molecules can be used. Such a description has been presented by Arecchi *et al.*[6] and by Glauber and Haake,[7] based on the use of the molecular collective states first introduced by Dicke.[8] In this treatment a coherent state is represented as a minimum-uncertainty wave packet (MUW) of all the collective states interacting with the radiation field. The quantum mechanical representation of coherent states as wave packets was first introduced by Glauber[9] in discussing coherence in the radiation field. This formalism was subsequently extended to the coherent states of spin and angular momentum systems,[10] and generalized to other Lie groups.[11] Quantum mechanical coherent states have the following properties: (1) They minimize the Heisenberg uncertainty relation; (2) they time evolve with a nonspreading wave function, and (3) they display a time-

dependent (oscillating) expectation value for an off-diagonal "displacement" operator (e.g., the electric field operator for coherent radiation states). At the same time such wave packets are the exact solutions of the equation of motion of a system driven by a classical (scalar) force; their use in discussing the forced harmonic oscillator,[12] as well as the radiation from a classical oscillating electric current,[13] is well known. The quantum mechanical representation of coherent states by MUW's, therefore, presents a natural language in describing a laser-driven multilevel system, such as a collection of two level molecules.

However, the relationship of the quantum mechanical model of coherence presented in Refs. 6 and 7 to the conventional description of coherent states through the statistical density matrix, its range of validity, as well as its applicability to the study of coherent optical phenomena have not been fully investigated. In this paper we try to elucidate these points by comparing the quantum mechanical model to the statistical concepts that are normally used in the study of coherent phenomena in matter, especially in the optical regime. We use a formalism developed in quantum optics in the discussion of the structure and time evolution of coherent states. This formalism underlines the difference between the quantum mechanical and statistical models and provides a convenient framework for describing optical experiments involving coherent states. The paper is organized as follows: In Sec. II we present a review of Dicke's formalism as an alternative to the statistical description of a collection of noninteracting molecules. In Sec. III we examine the case of a collection of molecules driven by a laser field, and investigate the relationship of the coherent states definable for such a system to the conventional (statistical) representation of coherent states in matter. Section IV contains a quantum mechanical view of the processes that a state may undergo as it loses its coherent characteristics. Section V is a discussion of coherence in macroscopic systems and molecular crystals, and Sec. VI presents the description of optical coherence-loss experiments within the quantum mechanical model. Finally, in Section VII we summarize our results and conclusions.

II. QUANTUM MECHANICAL COLLECTIVE STATES

A collection of N two-level molecules can be regarded as a single quantum mechanical system (rather than as a statistical ensemble of two-level systems, as is done conventionally) through the formalism developed by Dicke.[8] Since each molecule has two states, the collective Hamiltonian

$$\mathcal{K} = \sum_{j=1}^{N} \mathcal{K}_j \qquad (2.1)$$

has 2^N eigenstates. However, since the collection may contain only up to $N/2$ energy quanta, these eigenstates are highly degenerate. The Hamiltonian (2.1) is invariant under permutation of the individual molecules, implying that its eigenstates may be classified according to the

$$N! \Big/ \Big(\frac{N}{2}\Big)! \Big(\frac{N}{2}\Big)!$$

or

$$N! \Big/ \Big(\frac{N+1}{2}\Big)! \Big(\frac{N-1}{2}\Big)! \quad \text{if } N \text{ is odd}$$

irreducible representations of P_N, the permutation symmetry group of the Hamiltonian.

For example, there are N collective states containing a single excitation, and these are degenerate in the absence of intermolecular interactions. The basis set for single excitations which conforms to the permutation symmetry of the Hamiltonian consists of N orthonormal states $|1_m\rangle$ such that

$$|1_m\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \exp[2\pi i m j/N] |0_1 \cdots 1_j \cdots 0_N\rangle , \qquad (2.2)$$

with $0 \leqslant m \leqslant N-1$. The state $m = 0$ belongs to the totally symmetric representation of P_N and corresponds to the case in which all molecules have the same probability amplitude of being excited. For the case in which the N molecules occupy fixed positions in space $\{x_j\}$ related by the translational symmetry of a Bravais lattice, the N collective states of Eq. (2.2) are equivalent to the well-known Frenkel exciton states, with the correspondence

$$\mathbf{q} \cdot \mathbf{x}_j = 2\pi m j/N , \qquad (2.3)$$

where $\mathbf{q}$ is the wave vector.

An orthonormal basis set, invariant under P_N, may similarly be specified for the $N! /n! (N-n)!$ -dimensional space of n excitations.[14] These basis states can be written as appropriately phased superpositions of all the excited configurations of the collection containing n excitations. One such basis vector belongs to the totally symmetric representation of P_N and can be written as

$$|n\rangle = \left[\frac{n! (N-n)!}{N!}\right]^{1/2} \sum_{\text{configs.}} |0_1 \cdots \overbrace{1_j \cdots 1_j}^{n} \cdots 0_N\rangle .$$
$$(2.4)$$

Dicke has used a symmetry classification which rests on the formal similarity between the operators associated with collective excitations and those for angular momentum. This classification is not as complete as that of the permutation group but is sufficient for the treatment of the interaction of light with the collection, as it uniquely specifies all the states which are accessible by the radiation field.

Denoting by $\sigma_j^{\pm}$ the creation/annihilation operators for an excitation on the jth two-level molecule, we can write the collective operators which create/annihilate one excitation throughout the collection as

$$R^{\pm} = \sum_j \sigma_j^{\pm} . \qquad (2.5)$$

Interactions which may create an excitation with uniform probability amplitude throughout the collection (such as the radiative coupling for the case in which the collection is smaller in size than the wavelength of light) are describable by the operators $R^{\pm}$. The operator

$$R_z = \sum_j \sigma_j^z \qquad (2.6)$$

measures one half the population difference of ground and excited molecules, and together with $R^\pm$ follows angular momentum commutation rules

$$[R^+, R^-] = 2R_z , \qquad [R_z, R^\pm] = \pm R^\pm . \qquad (2.7)$$

The operator R^2 is defined as

$$R^2 = \tfrac{1}{2}(R^+R^- + R^-R^+) + R_z^2 . \qquad (2.8)$$

This operator commutes with $R^\pm$ and R_z as

$$[R^2, R_z] = 0 , \qquad [R^2, R^\pm] = 0 . \qquad (2.9)$$

The Hamiltonian for a collection of noninteracting molecules involves only the operator R_z

$$\mathcal{H} = \hbar\omega_0 \left(R_z + \frac{N}{2} \right) . \qquad (2.10)$$

Because of Eq. (2.9) the energy (occupation number) eigenstates are simultaneous eigenstates of R^2. The eigenvalues of R^2 may be written as $r(r+1)$; r may range from 0 (or from $\tfrac{1}{2}$ if N is odd) to $N/2$, and is referred to by Dicke as the "cooperation number." All the states with the same value of r constitute a cooperation manifold. The cooperation manifold $r = N/2$ consists of all the states which belong to the totally symmetric representation of P_N. There is one such state for each value of n, the occupation number, and it can be written in the form (2.4). The manifold $r = N/2$ consists of $N+1$ nondegenerate states including the collective ground state ($n = 0$) as well as the fully excited state of the collection ($n = N$). Manifolds with $r < N/2$ consist of states from several non-totally symmetric irreducible representations of P_N. The cooperation number may thus be taken as partial designation of the symmetry characteristics of each energy eigenstate, to the extent that it identifies uniquely the fully symmetric eigenstates ($r = N/2$), and that states of different r necessarily belong to different irreducible representations of P_N.

Since R^2 commutes with $R^\pm$, the collective creation/annihilation operators can relate only states within the same cooperation manifold. Following the formal analogy between a system of total angular momentum $j = N/2$ and the collective manifold $r = N/2$ composed of states of the form (2.4), we have

$$R^+ |n\rangle = \sqrt{(N-n)(n+1)} \, |n+1\rangle , \qquad (2.11a)$$

$$R^- |n\rangle = \sqrt{(N-n+1)n} \, |n-1\rangle , \qquad (2.11b)$$

and

$$|n\rangle = \left[\frac{(N-n)!}{N! \, n!} \right]^{1/2} (R^+)^n |0\rangle , \qquad (2.11c)$$

i.e., all the states that result from multiple (n) applications of the operator R^+ to the collective ground state belong to the nondegenerate manifold $r = N/2$. Therefore, in considering the radiative interaction of a collection of N molecules initially in their ground state, we may limit our attention to only *one* out of the $N!/n!(N-n)!$ possible collective states containing n excitations: the fully symmetric collective state $|n\rangle$ of Eq. (2.4). For crystals, and for the case $n = 1$, this is the familiar $q = 0$ rule for radiative transitions.

In Dicke's formalism the collective states of $r = N/2$ may be described through Eq. (2.4) as the "in-phase" superposition of the amplitudes of all possible configurations of n excitations in the collection of N molecules. They are highly "phase-correlated" states but are not quantum mechanical analogs of the statistical coherent states since they yield an expectation value of zero for the off-diagonal dipole operator $\hat{Q}_\pm = (R^+ + R^-)/2$ and do not display an oscillating macroscopic polarization.

In quantum optics, a state of the radiation field is said to be first-order coherent (and thus to be phase correlated) if its normalized first-order correlation function $g^{(1)}$ equals one (1) over all pairs of space-time points $(x_1 t_1; x_2 t_2)$, where

$$g^{(1)}(x_1 t_1; x_2 t_2) = |\langle \hat{E}^-(x_1 t_1)\hat{E}^+(x_2 t_2)\rangle| / [\langle \hat{E}^-(x_1 t_1)\hat{E}^+(x_1 t_1)\rangle \langle \hat{E}^-(x_2 t_2)\hat{E}^+(x_2 t_2)\rangle]^{1/2} . \qquad (2.12)$$

A perfectly monochromatic beam is first-order coherent independently of whether it is a laser or a conventional beam. Higher orders of coherence are similarly definable through higher-order correlation functions. A laser beam exhibits such higher orders of coherence, a feature closely related to the fact that it displays a nonzero expectation value for the electric field operator.

Given a state of a collection of N two-level molecules, we may define its degree of first-order coherences at molecules 1 and 2 located at $(x_1 t_1)$ and $(x_2 t_2)$, respectively, by analogy to quantum optics as

$$g^{(1)}(x_1 t_1; x_2 t_2) = |\langle \sigma_1^+(t_1) \sigma_2^-(t_2)\rangle| / [\langle \sigma_1^+(t_1)\sigma_1^-(t_1)\rangle_2 \langle \sigma_2^+(t_2)\sigma_2^-(t_2)\rangle]^{1/2} , \qquad (2.13a)$$

where the time evolution of the operators σ_i^+ occurs under the full Hamiltonian of the system. The average over the state of interest is denoted by $\langle \, \rangle$. If $x_1 \neq x_2$, the normalization of the correlation function is given by the conditional probability that molecule i is excited at t_i, given that j is unexcited at t_j. It can be calculated by expressing the state of interest at $t = t_j$ in the basis of excited molecular configurations and restricting the

averaging to those configurations in which j is unexcited; we denote that by $\langle \sigma_i^+ \sigma_i^-\rangle_j$. The *conditional* probability is used because we are dealing with a system composed of a finite number (N) of discrete excitable entities. In the limit that the number of excitations is much smaller than N, the conditional probability reduces to the ordinary probability as in Eq. (2.12) for the radiation field. Higher orders of coherence for col-

lective states may also be defined by similarly adapting the corresponding definitions from quantum optics. All eigenstates of the $r = N/2$ manifold can be shown to be first-order coherent, i.e., they are phase correlated for all pairs $(x_i t_i; x_j t_j)$. However, they do not necessarily exhibit higher orders of coherence, as is the case for quantum mechanical states that display a nonzero expectation value for the off-diagonal dipole operator (see Sec. III). The quantum mechanical superposition among the $r = N/2$ states and their statistical mixtures are also first-order coherent. There are also states outside the manifold $r = N/2$ which are first-order coherent, such as the states $n = 1$, $r = N/2 - 1$ which correspond to the $N - 1$ states with $m \neq 0$ in Eq. (2.2). Superpositions or statistical mixtures of $r = N/2$ states with states of other manifolds, however, do not display first-order coherence over all coordinate pairs $(x_i t_i; x_j t_j)$.

The concept of first-order coherence has been very widely used when discussing crystal states and processes.[15] In the theory of exciton migration, for example, a distinction is made between coherent (wave-like) motion of the excitation and incoherent (random hopping) transfer. The former case corresponds to first-order coherent states describable by a single wave vector, while the latter case consists of a statistical mixture of all wave vector states and thus lacks first-order coherence for pairs of points $(x_i; x_j)$ separated by more than a few lattice constants.

III. COLLECTIVE COHERENT STATES

A. The coherent excitation process

We consider a collection of N two-level molecules of energy $\hbar\omega_0$ driven by a coherent radiation field (laser or microwave) oscillating at a frequency ω. We assume that the state of the radiation remains coherent and undepleted throughout the interaction, so that the corresponding electric field is characterized by a well-defined oscillating expectation value of definite amplitude (E) and phase (ωt). If we further assume that all molecules experience the same field, we can describe the molecule–field interaction by a single c number, the Rabi frequency Ω. For example, in a collection driven by a laser field oscillating near a molecular absorption frequency, the Rabi frequency is given by

$$\Omega = \mu \cdot E/\hbar , \qquad (3.1a)$$

where μ is the molecular transition dipole, and it is assumed that the individual dipoles have on the average the same orientation with respect to E. Similarly, for a collection driven by two oscillating coherent fields (called incident and Stokes) whose frequency difference $\omega_I - \omega_s = \omega$ is near a vibrational resonance ω_0 of the individual molecules in the collection, the Rabi frequency is

$$\Omega = (\partial\alpha/\partial Q) E_I E_s /\hbar , \qquad (3.1b)$$

where $\partial\alpha/\partial Q$ is the differential polarizability of the molecules along the vibrational coordinate of interest.

The Hamiltonian of the laser-driven collection can then be written as

$$\mathcal{H} = \hbar\omega_0 \left(R_z + \frac{N}{2} \right) + \hbar\Omega(t)(R^+ e^{-i\omega t} + R^- e^{i\omega t}) , \qquad (3.2a)$$

where we have used the rotating wave approximation. The time dependence of the laser field amplitude (as, for example, when dealing with pulses) is included in $\Omega(t)$. For convenience we can take

$$\Omega(t) = 0 , \quad \text{for } t < 0 , \qquad (3.2b)$$

$$\Omega(t) = 0 , \quad \text{for } t > t_1 , \qquad (3.2c)$$

where t_1 is the time at which an observation is performed. Given the initial state of the collection at $t = 0$ (usually the collective ground state), the state reached at $t = t_1$ by driving the collection with a laser according to Eq. (3.2) is obtained by applying the corresponding time-evolution operator to the initial state

$$\psi(t_1) = \exp\left[-\frac{i}{\hbar} \int_0^{t_1} \mathcal{H}(\tau) d\tau \right] |0\rangle . \qquad (3.3)$$

It is in principle possible to evaluate Eq. (3.3) for the Hamiltonian (3.2) directly. The calculations are greatly simplified, however, if we note that Eq. (3.2a) can be partitioned as

$$\mathcal{H} = \mathcal{H}_1 + V(t) , \qquad (3.4)$$

where $\mathcal{H}_1$ is time independent. Using the well-known relationship between the time-evolution operators in the Schrödinger and interaction pictures, we can write Eq. (3.3) as

$$\psi(t_1) = \exp[- (i/\hbar)\mathcal{H}_1 t_1] \exp\left[-\frac{i}{\hbar} \int_0^{t_1} \bar{V}(\tau) d\tau \right] |0\rangle , \qquad (3.5a)$$

where

$$\bar{V}(\tau) = \exp[(i/\hbar)\mathcal{H}_1\tau] V(\tau) \exp[-(i/\hbar)\mathcal{H}_1\tau] . \qquad (3.5b)$$

In the conventional treatment of the interaction picture, the Hamiltonian (3.2a) is partitioned as

$$\mathcal{H}_1 = \hbar\omega_0 \left(R_z + \frac{N}{2} \right) . \qquad (3.6)$$

The final state $\psi(t_1)$ can then be written as

$$\psi(t_1) = \exp[- i\omega_0 t_1 [R_z + (N/2)]$$
$$\times \exp[- (\theta/2)(R^+ e^{i\phi_0} - R^- e^{-i\phi_0})] |0\rangle , \qquad (3.7a)$$

where

$$\theta e^{i\phi_0} = 2i \int_{-\infty}^{\infty} \Omega(t) \exp[i(\omega_0 - \omega)t] dt . \qquad (3.7b)$$

The limits of integration in Eq. (3.7b) can be extended to $\pm\infty$ because of Eqs. (3.2b) and (3.2c). The quantity θ represents the extent to which the collection is excited by the laser, and is largest when $\omega = \omega_0$, i.e., at resonance. In general, the detuning parameter $\Delta = \omega_0 - \omega$ will have a small imaginary part due to the linewidth of the molecular transition, so that θ is finite for small deviations from resonance also.

Another convenient way of partitioning the Hamiltonian is

$$\mathcal{H}_1 = \hbar\omega \left(R_z + \frac{N}{2} \right) , \qquad (3.8)$$

which corresponds to the "rotating frame representa-

tion" of magnetic resonance. The advantage of this partitioning is that for the case in which the driving force (Rabi frequency) is constant in time

$$\Omega(t) = \Omega \ , \quad \text{for} \ 0 \leqslant t \leqslant t_1 \ , \tag{3.9}$$

the evolution of $\bar{V}(t)$ in the rotating frame is time independent, i.e., combining Eqs. (3.8) and (3.5b), we have

$$\bar{V}(\tau) = \hbar\Delta \left(R_z + \frac{N}{2} \right) + \hbar\Omega (R^+ + R^-) \ . \tag{3.10}$$

The rotating-frame Hamiltonian (3.10) can be diagonalized exactly by a unitary transformation of the form e^S with

$$S = \left(\frac{R^- - R^+}{2} \right) \arctan\left(\frac{2\Omega}{\Delta} \right) \ , \tag{3.11a}$$

i.e.,

$$e^S \bar{V} e^{-S} = \hbar \sqrt{\Delta^2 + 4\Omega^2} \ , \quad R_z \equiv \tilde{\bar{V}} \ . \tag{3.11b}$$

This mathematical formulation leads to a geometrical interpretation of the coherent excitation process, analogous to that used in magnetic resonance. Since $e^{-i\mathcal{K}_1 t}$ is the unitary transformation which transforms the "rotating" frame into the "laboratory" frame, we can write the final state (after coherent excitation) observed in the rotating frame as

$$\exp\left[(i/\hbar)\mathcal{K}_1 t_1 \right] \psi(t_1) = e^{-S} \exp[-i\tilde{\bar{V}} t] e^S |0\rangle \ , \tag{3.12}$$

i.e., the coherent excitation process in the rotating frame can be considered as a simple time evolution $(e^{-i\tilde{\bar{V}} t})$ of the initial state of the collection $|0\rangle$ at a frequency $\sqrt{\Delta^2 + 4\Omega^2}$ for a time t_1 around a new "axis of quantization" which forms an angle of $\arctan(2\Omega/\Delta)$ with the "old" axis. As in the geometric picture of magnetic resonance, the new axis is given by the vector sum of the old quantization axis and the driving field in the rotating frame. In this interpretation of Eq. (3.12), the unitary transformations e^{-S} and e^S can be considered as relating the collective states in the two axis systems.

B. The quantum mechanical and statistical coherent states

The state prepared in a collection of initially unexcited two-level molecules through their interaction with a coherent electromagnetic field (such as a laser) can be written as a superposition of all the occupation states of the $r = N/2$ manifold, according to Eq. (3.7):

$$\| \theta \rangle = \exp\left[-\frac{\theta}{2} (e^{i\phi} R^+ - e^{-i\phi} R^-) \right] |0\rangle \ , \tag{3.13a}$$

$$= \left(\cos \frac{\theta}{2} \right)^N \exp\left(e^{i\phi} \tan \frac{\theta}{2} R^+ \right) |0\rangle \ , \tag{3.13b}$$

$$= \left(\cos \frac{\theta}{2} \right)^N \sum_{n=0}^{\infty} \left[\left(e^{i\phi} \tan \frac{\theta}{2} \right)^n \sqrt{\frac{N!}{n!(N-n)!}} \right] |n\rangle \ , \tag{3.13c}$$

where $|n\rangle$ are the totally symmetric collective eigenstates corresponding to n excitation quanta in the collection, as defined in Eq. (2.4). Equation (3.13c) follows from Eq. (3.13b) by use of Eqs. (2.11), while the equality of Eqs. (3.13a) and (3.13b) is shown in Ref. 6. This

state is formally analogous to the quantum mechanical coherent state $\|\theta, \phi\rangle$ in a system of total angular momentum $j = N/2$ (generated by "tipping" the wave function of the ground state $|j, -j\rangle$ through an azimuthal angle θ, and rotating about the z axis through an angle $\phi)$[10,11]:

$$\| \theta, \phi \rangle = \left(\cos \frac{\theta}{2} \right)^{2j}$$

$$\times \sum_{m=-j}^{j} \left[\left(e^{i\phi} \tan \frac{\theta}{2} \right)^{m+j} \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} \right] |j, m\rangle \ , \tag{3.14a}$$

for which the uncertainty relation

$$\langle j_x^2 \rangle \langle j_y^2 \rangle \geqslant \langle j_z^2 \rangle / 4 \tag{3.14b}$$

is minimized, i.e., the equality sign holds.

The state produced in a collection of molecules driven by a coherent electromagnetic field is therefore a minimum-uncertainty wave packet (MUW) of all the collective states accessible to the radiation, and its properties are thus generally analogous to those of the Glauber wave packet for the harmonic oscillator[9]: The mean number of excitations present in the wave packet is

$$\bar{n} = \langle \theta \| \left(R_z + \frac{N}{2} \right) \| \theta \rangle = N \sin^2 \frac{\theta}{2} \ , \tag{3.15}$$

while the dipole operator has a nonzero expectation value (macroscopic polarization)

$$Q_{\pm} = \langle \theta \| \frac{R^+ \pm R^-}{2} \| \theta \rangle$$

$$= N \sin \frac{\theta}{2} \cos \frac{\theta}{2} \left(\frac{e^{i\phi} \pm e^{-i\phi}}{2} \right) \ . \tag{3.16}$$

If after the excitation process the collection evolves in time under the Hamiltonian of Eq. (2.10), the macroscopic polarization varies in an oscillatory manner with

$$\phi = \omega_0 t + \phi_0 \ , \tag{3.17}$$

while its amplitude remains constant. The number of excitation quanta in the coherent state (3.13) cannot be known exactly; the uncertainty (variance) in that number is

$$(\Delta \bar{n})^2 = \langle \theta \| \left(R_z + \frac{N}{2} \right)^2 \| \theta \rangle - \langle \theta \| \left(R_z + \frac{N}{2} \right) \| \theta \rangle^2$$

$$= N \sin^2 \frac{\theta}{2} \cos^2 \frac{\theta}{2} \ , \tag{3.18}$$

and is independent of time as long as the wave packet evolves in time under the Hamiltonian of Eq. (2.10): its wave function does not spread and it retains its minimum uncertainty characteristics. The MUW of Eq. (3.13), therefore, may be considered as a quantum mechanical representation of a coherently excited state in a collection of molecules, in direct analogy to the coherent states of the radiation field.[9]

Conventionally, a coherent state of a collection of identical two-level molecules is represented by the ensemble-averaged density matrix of the individual molecules[1]:

$$\rho = \begin{bmatrix} \sin^2 \frac{\theta}{2} & \sin \frac{\theta}{2} \cos \frac{\theta}{2} \exp[-i\omega_0 t - i\phi_0] \\ \sin \frac{\theta}{2} \cos \frac{\theta}{2} \exp[i\omega_0 t + i\phi_0] & \cos^2 \frac{\theta}{2} \end{bmatrix} . \qquad (3.19)$$

In optical phenomena, it is customary to discuss the time evolution of the density matrix (3.19) in the Feynman–Vernon–Hellwarth (FVH) representation,[3] thus using a common language with NMR: The statistically averaged expectation values of the off-diagonal (displacement) operators σ_x and σ_y, i.e.,

$$\text{tr}(\rho\sigma_x) = \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos(\omega_0 t + \phi_0) , \qquad (3.20a)$$

$$\text{tr}(\rho\sigma_y) = \sin \frac{\theta}{2} \cos \frac{\theta}{2} \sin(\omega_0 t + \phi_0) , \qquad (3.20b)$$

respectively, together with the population difference

$$\text{tr}(\rho\sigma_z) = \frac{1}{2} \left(\sin^2 \frac{\theta}{2} - \cos^2 \frac{\theta}{2} \right) , \qquad (3.20c)$$

are regarded as the three components of a pseudo-spin vector which is tipped by an angle θ with respect to the z axis while at the same time it precesses about that axis, thereby describing a phase for the time evolution of the coherent polarization.

Both models of coherence (i.e., in terms of the MUW or in terms of the statistical density matrix) meet the requirements for the representation of a coherent state: the relevant dipole operator has a nonzero expectation value corresponding to the macroscopic polarization whose oscillatory motion defines a measurable phase. The phase and amplitude of this oscillation are preserved as long as the system remains in the same state. In both models, the values of all observables are obtained as averages over the coherent state. However, in the case of the MUW, averaging is due to the quantum mechanical uncertainty inherent in the wave packet, while in the two-dimensional density matrix formalism it is thought to be due to the statistical averaging over the ensemble of molecules.

The MUW contains all the information available in the statistical representation of the coherent state: the three components of the FVH vectorial model are given by the expectation values of the corresponding operators in Eqs. (3.15) and (3.16). Thus, any situation which is usually discussed in terms of the statistical density matrix and the FVH vectorial model can be treated in terms of the quantum mechanical representation of the coherent state. In addition to this information, however, the MUW of Eq. (3.13) contains quantum mechanical information which is unavailable in the statistical model as shown in the following examples.

The uncertainty relations that are central to the MUW model are not even applicable in the statistical model: The uncertainty in the number of excitation quanta in the MUW calculated in Eq. (3.18) is directly related to the mean number of excitations present, as in the case of the Glauber wave packets for the radiation field.[9] For an arbitrary collective quantum mechanical state,

this relationship does not necessarily hold; it is a property of coherent states so that together with the uncertainty in the phase it minimizes the number-phase uncertainty relation. In the statistical model, however, *any* state of the ensemble represented by a two-level density matrix with a given average number of excitations has the *same* uncertainty, whether the state is coherent or not:

$$(\Delta\bar{n})^2 = \text{tr}[\rho(\sigma_z + \tfrac{1}{2})^2] - [\text{tr}\rho(\sigma_z + \tfrac{1}{2})]^2 = \rho_{\text{II}} - \rho_{\text{II}}^2 . \qquad (3.21)$$

The multilevel nature of collective states permits the characterization of such states through different orders of correlation functions, analogous to those used in quantum optics to describe all possible photon interference experiments. A hierarchy of orders of coherence characterizing fully the collective coherent state may be defined in terms of these correlation functions, which can then be evaluated completely within the quantum mechanical representation of the coherent state (3.13) (i.e., with no external assumptions). A coherent state can be shown to have a degree of coherence of one (1) to all N orders definable for an N molecule collection, while all other states will lack one or more orders of coherence. For excitations described by a two-level density matrix, on the other hand, the definition and evaluation of such correlation functions are not possible unless additional assumptions concerning the ensemble are invoked. The most common assumption is that of a Markoffian interaction with a heat bath, which permits the use of such techniques as the quantum regression theorem.[16] The only quantities that can be directly evaluated in an ensemble of two-level molecules are the one-time averages of the dipole and number operators [Eqs. (3.20)]; these are therefore the only experimental observables by which a state of a statistical ensemble can be characterized.

The description of quantum mechanical effects, such as spontaneous emission, is very awkward within the statistical model. As an example, we shall calculate the light emission intensity from a coherent state of an ensemble of molecules. The intensity of the coherent emission is proportional to the square of the macroscopic polarization of the emitting state; the total polarization in an ensemble of N molecules, all in phase, is given from Eq. (3.19) as

$$P(t) = N(\mu \cdot E)\text{tr}(\rho\sigma^-) \qquad (3.22a)$$

so that the emitted intensity for a coherent ensemble is obtained from Eq. (3.19) as

$$|P(t)|^2 = I = N^2(\mu \cdot E)^2 \sin^2 \frac{\theta}{2} \cos^2 \frac{\theta}{2} . \qquad (3.22b)$$

However, for a fully inverted system, $\theta = \pi$, which implies that such a system cannot emit. The presence of spontaneous emission clearly contradicts this conclusion. On the other hand, the proper quantum me-

chanical procedure to calculate the probability of emission (light intensity) is not to square the expectation value of σ^- but rather to take the expectation value of the "squared" operator $\sigma^+\sigma^-$. Then the emission probability in an ensemble of N molecules is

$$I = N(\mu \cdot E)^2 \sin^2 \frac{\theta}{2} \ . \tag{3.23}$$

This equation gives a finite value of I for a fully inverted system, but cannot predict the emission from a coherent state since the value of I is independent of the off-diagonal elements of the density matrix. No such problem, however, arises when the description of the coherent state is done in quantum mechanical terms according to Eq. (3.13). The intensity is given by

$$I = (\mu \cdot E)^2 \langle \theta | | R^+ R^- | | \theta \rangle$$

$$= (\mu \cdot E)^2 \left[N(N-1) \sin^2 \frac{\theta}{2} \cos^2 \frac{\theta}{2} + N \sin^2 \frac{\theta}{2} \right], \tag{3.24}$$

where both the coherent (almost classical) and the quantum mechanical emissions are incorporated. For a fully inverted system the quantum mechanical emission dominates, while for any other coherent state the classical term is larger.

C. Validity of the quantum mechanical and statistical models

The relationship of the statistical and quantum mechanical representations of a coherent state is clarified by writing the MUW of Eq. (3.13) in a local representation in terms of individual molecular states. Using the commutativity of operators belonging to different molecules, we find

$$|| \theta \rangle = \prod_{j=1}^{N} \left\{ \cos \frac{\theta}{2} \ |0\rangle_j + e^{i\phi} \sin \frac{\theta}{2} \ |1\rangle_j \right\} \ . \tag{3.25}$$

Thus, in a minimum uncertainty wave packet, the excitation may be considered as equally distributed in amplitude and phase on all molecules. While this is reminiscent of the conventional representation of a coherent state in an ensemble, there is one important difference: The conventional coherent state is a statistical state composed of the individual molecular superpositions and is thus expressible through a two-dimensional density matrix. The MUW of Eqs. (3.13) and (3.25), on the other hand, is a pure quantum mechanical state expressible as the *product* of N identical molecular wave functions. The MUW involves an $N+1$-dimensional state space and the operators corresponding to its observable manifestations must be represented as $(N+1) \times (N+1)$ matrices; the conventional coherent state, on the other hand, has a two-dimensional state space as can be seen from the 2×2 statistical density matrix through which it is usually described. The reduced dimensionality of the conventional coherent state (which arises from the consideration of the molecular collection as a statistical ensemble) obscures many manifestations of the quantum mechanical nature of collective coherent states: In the statistical model, a many-time many-particle correlation function is separable into the corresponding product of one-particle one-time

functions. For example, the second-order correlation function describing an experiment of probability interference between the excitations on two molecules (equivalent to the Hanbury, Brown, and Twiss experiment in quantum optics) is evaluated in the statistical model as

$$\langle \sigma_2^+(t_2)\sigma_1^+(t_1)\sigma_1^-(t_1)\sigma_2^-(t_2) \rangle - \langle \sigma_2^+\sigma_2^- \rangle \langle \sigma_1^+\sigma_1^- \rangle \ , \tag{3.26}$$

yielding the same result ρ_{ii}^2 both for coherent and for incoherent states. Within the quantum mechanical model this separability is rigorous either (1) if the collection is in a fully coherent state [Eq. (3.25)] or (2) if the commutator relation

$$[\sigma_2^+(t_2), \ \sigma_1^-(t_1)] = 0 \tag{3.27}$$

is satisfied. This latter condition would be true if the excitations on sites 1 and 2 were measurable independently, i.e., if the molecules were isolated from each other and from their environment so that the full Hamiltonian describing the experimental system were that of Eq. (2.10). In general, however, the Hamiltonian involves a coupling of the molecules with each other, either directly (as in crystals) or to second order through the interaction of each molecule with the radiation field. The value of the commutator (3.27) is related to the probability amplitude for transfer of an excitation between molecules 1 and 2 at the corresponding times. For normal NMR and ESR situations and for $(t_2 - t_1)$ within time scales of experimental interest, this transfer is often negligible, indicating that the statistical model constitutes an adequate description of such systems. The same also holds for optical experiments in low-pressure gases or very dilute crystal impurities. In condensed phases, however, molecules communicate with each other in times of the order of $10^{-9}-10^{-13}$ s so that the statistical model is often inadequate even for many simple experiments. For example, the statistical model cannot account for the spectrum of light resonantly scattered from a collection of two-level molecules, since this spectrum is given by a two-time first-order correlation function, a quantity which is not obtainable directly from the statistical density matrix. One simple way to obtain such a correlation function within the statistical model[17] is to invoke a Markoffian interaction with a heat bath and then use the quantum regression theorem[16] to relate the two-time correlation function to one-time ensemble averages obtainable from the density matrix. These additional Markoffian conditions constitute simply a statistical simulation of quantum mechanical uncertainty and thus help reintroduce into the ensemble the molecular correlations which are suppressed when the collection is treated mathematically as a statistical ensemble. Within the quantum mechanical model, of course, no additional assumptions are required to calculate the two-time first-order correlation function.

The two-dimensional statistical density matrix, then, may be expected to provide a good description of the excited states in a collection of molecules if (1) the commutator of Eq. (3.27) is small enough that cooperative effects among molecules may be neglected and the collection of molecules may be reasonably approximated by a classical statistical ensemble, or if (2) the collec-

tion is in a fully coherent state, in which case the two-dimensional density matrix may be considered simply as a "shorthand notation" for the product of N identical molecular wave functions composing the MUW.

IV. THE TIME EVOLUTION OF A COHERENT EXCITATION

Within the statistical model, coherence is lost and the macroscopic oscillating polarization decays if stochastic fluctuations in the ensemble cause a randomization of the phases of the individual two level excitations (T_2' process). A coherent state may also decay if the population in the ensemble relaxes to its thermal equilibrium value (T_1 process).

Within the quantum mechanical model, population relaxation occurs when the Hamiltonian

$$\mathcal{H} = \hbar \omega_0 \left(R_z + \frac{N}{2} \right) + H' \tag{4.1}$$

includes in H' non-energy-conserving interactions between the collection and a heat bath, so that there is a decay of the expectation value of the average number of excitation quanta in the collection:

$$\bar{n}(t) = \langle \theta | | e^{i\mathcal{H}t} \left(R_z + \frac{N}{2} \right) e^{-i\mathcal{H}t} | | \theta \rangle . \tag{4.2}$$

The macroscopic oscillating polarization, on the other hand,

$$Q_{\pm}(t) = \langle \theta | | e^{i\mathcal{H}t} \left(\frac{R^+ \pm R^-}{2} \right) e^{-i\mathcal{H}t} | | \theta \rangle \tag{4.3}$$

decays if the time evolution of the coherent wave packet $||\theta\rangle$ involves the loss of its minimum uncertainty characteristics. The reason is, of course, that an MUW is the only quantum mechanical state for which the dipole operator has a finite expectation value. Therefore, loss of the minimum uncertainty characteristics may include processes other than those describable as a "phase randomization."

The interaction Hamiltonians H' that cause T_1 or T_2' processes can be characterized by their commutation properties: In general, a Hamiltonian that commutes with the population-difference operator

$$[H, R_z] = 0 \tag{4.4}$$

and whose commutator with the collective creation/annihilation operators is proportional to those operators

$$[H, R^+] = \alpha R^+ , \tag{4.5a}$$

$$[H, R^-] = -\alpha^* R^- , \tag{4.5b}$$

(where α is a c number) retains a constant expectation value for the population (4.2), while it produces a sinusoidal oscillation for the polarization (4.3). Such is the case of the zeroth-order Hamiltonian of Eqs. (4.1) or (2.10), which corresponds to the situation in which there are no interactions among the molecules in the collection, or between the collection and a heat bath.

If H' does not commute with R_z, it produces a temporal variation of the average number of excitation quanta in the collection (4.2). A time evolution of the

macroscopic polarization (4.3) other than simple cyclic motion is associated with an interaction H' which violates Eqs. (4.5). In general, any time evolution involves recurrences dependent on the form of the eigenvalue spectrum of H [Eq. (4.1)]. In the limit that this spectrum constitutes a continuum, the time evolution of the population and/or the polarization involves a decay, giving rise to the equivalent of T_1 and T_2 processes of the statistical model.

Rewriting the commutation relation of H' with R_z as

$$C = [H', R_z] = \frac{1}{2} [[H', R^+], R^-] - \frac{1}{2} [[H', R^-], R^+] , \tag{4.6}$$

we note that $C \neq 0$ implies that Eqs. (4.5) cannot be satisfied by H'. This indicates that a population decay produces a decay of the macroscopic polarization. On the other hand, if H' violates Eqs. (4.5), we may still have $C = 0$, if the commutator

$$D \equiv [[H', R^+], R^-] \tag{4.7}$$

is Hermitian. In that case, we have

$$C = \frac{1}{2}(D - D^\dagger) = 0 . \tag{4.8}$$

This indicates that a decay of the macroscopic polarization does not necessarily involve a population decay, as is also the case for T_2' relaxation in the statistical model.

For a coherence loss process in which there is no population decay, Eq. (4.4) implies that

$$[H', R_z^n] = 0 \tag{4.9}$$

for all exponents n, i.e., transverse relaxation leaves all the moments of the energy distribution unchanged. In other words, the only (incoherent) states that may result from the loss of the minimum uncertainty characteristics of a coherent wave packet are those in which states of different occupation numbers have binomial weights, i.e., have the same distribution as in the MUW of Eq. (3.13). Examples of such states are (1) statistical mixed states involving the occupation eigenstates of the $r = N/2$ manifold, e.g.,

$$\rho^{(1)}(\theta) = \left(\cos^2 \frac{\theta}{2} \right)^N \sum_{n=0}^{N} |n\rangle \frac{N!}{n!(N-n)!} \left(\tan^2 \frac{\theta}{2} \right)^n \langle n| , \tag{4.10}$$

(2) quantum mechanical superpositions or statistical mixed states involving occupation states from several cooperation manifolds, e.g., if H' involved scattering of the excitation into all permutation-symmetry states equally, the resulting incoherent state would be

$$\rho^{(2)}(\theta) = \left(\cos^2 \frac{\theta}{2} \right)^N \sum_{n=0}^{N} \left(\tan^2 \frac{\theta}{2} \right)^n$$

$$\times \sum_{r=|N/2-n|}^{N/2} \sum_{\alpha=1}^{s_r} |n, r, \alpha\rangle \langle \alpha r n| , \tag{4.11}$$

where α is an additional quantum number which specifies the permutation symmetry of a state within each r manifold. There are

$$g_r = \frac{N!\,(2r+1)}{\left(\dfrac{N}{2}+r+1\right)!\left(\dfrac{N}{2}-r\right)!} \qquad (4.12a)$$

values of α in the rth manifold[8] so that there are

$$\frac{N!}{n!\,(N-n)!} \qquad (4.12b)$$

values of r and α for each n.

Experimentally, coherence loss can be followed by monitoring the decay of the macroscopic polarization. Within the statistical model, this single measurable quantity characterizes completely T_2 relaxation, since coherence loss can only be described as a phase randomization among the constituents of the ensemble. Within the quantum mechanical model, however, this single observable does not suffice, since it simply indicates the *overall* loss of the minimum uncertainty characteristics of the coherent wave packet. The coherent state may decay in an infinity number of ways, each one resulting in a different type of incoherent state. The incoherent states of the form (4.10) are first-order coherent, i.e., they are the result of the decay of coherence to all orders *except the first*. Processes that produce states of the form (4.11) do not preserve coherence to any order. Within the quantum mechanical model, therefore, T_2 processes can be distinguished with respect to their effect on the different orders of coherence of the MUW. This suggests the possibility of monitoring the different ways in which a coherent state loses its minimum uncertainty characteristics by following the relaxation of the different orders of coherence through experiments analogous to those in quantum optics.[18]

The distinction between interactions H' which destroy coherence to all orders and those that cause a decay of the macroscopic polarization while preserving first-order coherence can be seen theoretically through the commutation properties of H'. In the discussion of Eq. (2.13) it was noted that the eigenstates of the $r = N/2$ manifold are first-order coherent, while their superpositions or statistical mixtures with states of other manifolds are not. Thus, an interaction which preserves first-order coherence does not mix states of different manifolds. It therefore preserves r as a good quantum number of the collection and

$$[H',\ R^2] = 0 \ . \qquad (4.13)$$

On the other hand, an interaction H' that destroys first-order coherence must mix different cooperation manifolds, and thus does not commute with R^2. If H' violates Eq. (4.13), it must also violate Eqs. (4.5). This indicates that an interaction which destroys first-order coherence necessarily causes the decay of the macroscopic polarization. The converse is not always true: An interaction that does not follow Eqs. (4.5) may still commute with R^2, as, for example, the case $H' = R^+R^-$:

$$[H',\ R^+] = 2R^+R_z \ . \qquad (4.14)$$

The process of coherence loss through the decay of all orders of coherence can be considered as the closest

TABLE I. Commutation rules for relaxation.

Commutation relation	Physical process
(1) $[H',\ R_z] \neq 0$	Population decay (T_1)
(2) $[H',\ R^\pm] \neq \alpha R^\pm$	Displacement (polarization) decay (T_2)
(3) $[H',\ R^2] \neq 0$	Decay of all orders of coherence
(1) always implies (2)	Population decay always causes polarization decay
(2) does not always imply (1)	Polarization decay is not always accompanied by population decay
(3) always implies (2)	Decay of all orders of coherence always causes polarization decay
(2) does not always imply (3)	Polarization may decay, retaining one or more orders of coherence

quantum mechanical analog of the phase randomization process in the statistical model. The reason is that states belonging to different cooperation manifolds correspond to excited states with a different phase distribution in the probability amplitude of the excited configurations that compose them. Thus, the quantum mechanical process which most closely corresponds to the statistical T_2 process through dynamic dephasing is the scattering of the $r = N/2$ eigenstates into all other cooperation manifolds. Within the quantum mechanical model, such "complete phase randomization" is only one of the possible T_2 processes which bring about the decay of the coherent state. The completely phase randomized situation consists of a mixture of all collective states such that all phase distributions have equal weights as in Eq. (4.11). A MUW may also decay through processes which preserve one or more orders of coherence, and which have no equivalent in the statistical model. These results are summarized in Table I.

V. COHERENCE IN MACROSCOPIC COLLECTIONS OF MOLECULES

In the preceding discussion it was assumed that the spatial extent of the collection of molecules is smaller than the wavelength of light. In most situations of experimental interest, however, the collection of molecules is macroscopic so that upon interaction with a mode of the electromagnetic field it is excited into a collective state bearing the phase structure of the radiation mode. The interaction of the sample with a radiation mode of wave vector k can be described by the operators

$$R_k^+ = \sum_j \sigma_j^+ e^{ikr_j} \ , \qquad (5.1a)$$

$$R_{-k}^- = \sum_j \sigma_j^- e^{-ikr_j} \ , \qquad (5.1b)$$

which create/annihilate an excitation in the medium

with no knowledge as to its location, but with a phase dependent on its position. Since the operators $R_{\pm k}^{\pm}$ do not commute with R^2, the states produced by successive applications of R_k^+ to the collective ground state are not restricted to the manifold of cooperation number $r = N/2$, if described in the eigenstate basis of Sec. II. However, since R_k^+, R_{-k}^-, and R_z follow angular momentum commutation relations similar to those of Eq. (2.7), it is possible to define an operator R_k^2 analogous to R^2 in Eq. (2.8) and thus redefine the cooperation eigenstates and their manifolds. Because of the commutation relation

$$[R_{\pm k}^{\pm}, \ R_k^2] = 0 \ , \tag{5.2}$$

the states resulting from successive applications of $R_{\pm k}^{\pm}$ to the collective ground state can be described in this new eigenstate basis as a linear superposition of only the eigenstates within the cooperation manifold $r_k = N/2$. States of this manifold have first-order molecular coherence, as defined in Eqs. (2.13). Fully coherent states created in the collection by a radiation mode of wave vector k can be described as minimum-uncertainty wave packets of all the occupation-number states of the manifold $r_k = N/2$, as in Eq. (3.13):

$$|| \theta_k \rangle = \left(\cos \frac{\theta}{2} \right)^N \exp[i\phi \tan(\theta/2) R_k^+] \, |0\rangle$$

$$= \left(\cos \frac{\theta}{2} \right)^N \sum_{n=0}^{N} \left(e^{i\phi} \tan \frac{\theta}{2} \right)^n \sqrt{\frac{N!}{n!(N-n)!}} \, |n_k\rangle \ , \tag{5.3}$$

or in the local representation in a manner analogous to Eq. (3.25):

$$|| \theta_k \rangle = \prod_{j=1}^{N} \left(\cos\frac{\theta}{2} \, |0\rangle_j + \exp[i\phi + ikr_j] \sin \frac{\theta}{2} \, |1\rangle_j \right) \ . \tag{5.4}$$

In general, the formalism developed in the preceding sections for uniform collective excitations (i.e., with no phase structure) if appropriately modified holds also for the collective states of macroscopic collections of molecules.

Molecular crystals present a particularly interesting type of macroscopic collections of molecules, in that the molecules that compose them are arranged in a spatially periodic structure. This implies that it is possible to define a set of N phased collective operators which are invariant under the space group of the lattice

$$R_{\pm q}^{\pm} = \sum_{j=1}^{N} \sigma_j^{\pm} e^{\pm iqr_j} \ . \tag{5.5}$$

The crystal couples to the radiation field through only one pair of operators $R_{\pm q_0}^{\pm}$ for each direction, satisfying $q_0 = k$ while at the same time satisfying the resonance condition with the radiation mode. Because of the small dimensions of the unit cell as compared to the wavelength of light, this condition is often approximated as $q_0 = 0$. The cooperation operator relevant to an optical experiment is $R_{q_0}^2$. The N orthonormal states obtained by applying each R_q^+ to the collective ground state

$$|1, \, q\rangle = R_q^+ |0\rangle \tag{5.6}$$

form a complete basis set which spans the state space of a single excitation. These are the familiar Frenkel exciton states used in the theory of molecular crystals. The state $|1, \, q_0\rangle$ belongs to the cooperation manifold $r_{q_0} = N/2$ while all others have $r_{q_0} = (N/2) - 1$. Multiple applications of the operators (5.5) to the collective ground state result in overcomplete sets of nonorthogonal states. For example, there are N^2 states obtained by applying the operator $R_q^+ R_p^+$ to the ground state, yet the state space of two excitations is only $N(N-1)$ dimensional. Excitons therefore are not a good basis for the description of crystal states containing more than one excitation. Use of exciton states in the description of multiply excited crystals gives rise to dynamical and kinematic interactions among the excitons, as in the theory of magnons.[19]

The Hamiltonian of a crystal which can be described as a collection of two-level molecules with an intermolecular interaction that delocalizes the intramolecular excitation is

$$\mathcal{H} = \sum_{j=1}^{N} \hbar\omega_0 (\sigma_j^z + \tfrac{1}{2}) + \sum_{j \neq l} \hbar\gamma_{jl} \sigma_j^+ \sigma_l^- \ . \tag{5.7}$$

Since the operators (5.5) form a complete set, they can be used to describe the molecular operators

$$\sigma_j^{\pm} = \frac{1}{N} \sum_{q=0}^{2\pi/a} R_{\pm q}^{\pm} e^{\mp iqr_j} \ . \tag{5.8}$$

Substituting Eq. (5.8) into Eq. (5.7), we obtain for the case in which γ_{jl} depends only on the distance $r_j - r_l$ between the two interacting molecules

$$\mathcal{H} = \hbar\omega_0 [R_z + (N/2)] + \frac{\hbar}{N} \sum_{q=0}^{2\pi/a} J(q) R_q^+ R_{-q}^- \ , \tag{5.9a}$$

where

$$J(q) = \frac{1}{N} \sum_{l \neq j} \gamma_{jl} \exp[-iq(r_l - r_j)] \ . \tag{5.9b}$$

This Hamiltonian displays some features similar to those discussed in the quantum mechanical view of the coherence loss process in Sec. IV. The intermolecular interaction term H' commutes with the population difference operator R_z:

$$[H', \ R_z] = 0 \ , \tag{5.10}$$

while its commutator with the optical polarization operator $R_{-q_0}^-$ is

$$[H', \ R_{-q_0}^-] = \frac{2\pi}{N} \sum_{q'=0}^{2\pi/a} J(q') R_{z(q'-q_0)} R_{-q'}^- \neq \alpha R_{-q_0}^- \ . \tag{5.11}$$

This implies that if a coherent state $|| \theta_{q_0} \rangle$ of the form (5.3) and (5.4) is prepared in a molecular crystal through its interaction with a laser or microwave field, that state may lose its minimum uncertainty characteristics because of intermolecular interactions, while the excitation energy in the crystal is conserved. The operator H' may be separated into two parts

$$H' = \frac{\hbar}{N} J(q_0) R_{q_0}^+ R_{-q_0}^- + \frac{\hbar}{N} \sum_{q \neq q_0} J(q) R_q^+ R_{-q}^- \equiv H_1' + H_2' \ , \tag{5.12}$$

which follow different commutation relations with respect to the cooperation operator:

$$[H'_1, R^2_{q_0}] = 0 \tag{5.13a}$$

and

$$[H'_2, R^2_{q_0}] \neq 0 , \tag{5.13b}$$

i.e., H' causes the decay of the coherent polarization both through interactions which destroy coherence to all orders [Eq. (5.13b)] and through interactions that preserve first-order coherence [Eq. (5.13a)]. We note, however, that since the spectrum of H'_1 is discrete, the temporal variation of the coherent polarization due to that term alone has finite recurrencies.

In the usual treatment of molecular crystals it is assumed that the crystal is very weakly excited, i.e., the average number of excitations present is much smaller than N so that the small-amplitude approximation can be invoked in writing the crystal Hamiltonian. Within this approximation and by use of the Holstein–Primakoff transformation,[19] the angular-momentum-type collective operators contract into the corresponding Bose creation/annihilation operators, i.e.,

$$\frac{1}{\sqrt{N}} R^\pm_{\pm q} \rightarrow B^\pm_{\pm q} , \tag{5.14}$$

where B^+_q / B^-_{-q} follow Bose commutation relations. Since

$$\hbar \omega_0 \sum_{j=1}^{N} (\sigma^z_j + \tfrac{1}{2}) = \frac{1}{N} \hbar \omega_0 \sum_{q=0}^{2\pi/a} R^+_q R^-_{-q} , \tag{5.15}$$

we can write the Hamiltonian of Eq. (5.9) in the small-amplitude approximation as

$$\mathcal{H}_{SA} = \sum_{q=0}^{2\pi/a} \hbar [\omega_0 + J(q)] B^+_q B^-_{-q} , \tag{5.16}$$

which is the familiar molecular exciton Hamiltonian. Under this approximation, the MUW of Eq. (5.3) have been shown to contract into the Glauber wave packet of the corresponding boson states.[6] Thus, a small-amplitude coherent state prepared in a crystal through an optical process is

$$||\beta\rangle = e^{-\beta^2/2} \sum_{n=0}^{\infty} \frac{(e^{i\phi_0}\beta)^n}{\sqrt{n!}} |n_{q_0}\rangle , \tag{5.17}$$

where

$$\beta = \sqrt{N} \theta/2 , \quad \text{for } \theta \ll 1.$$

In the local representation

$$||\beta\rangle = \prod_{j=1}^{N \to \infty} \left[\left(1 - \frac{\beta^2}{2}\right)|0\rangle_j + \beta \exp[i\phi_0 + iq_0 r_j]|1\rangle_j \right] . \tag{5.18}$$

We note that in the small-amplitude approximation, operators belonging to different q values commute, implying that the exciton description of multiply excited crystal states is assumed to be good. It also means that the small-amplitude MUW of Eq. (5.17) does not lose its minimum-uncertainty characteristics as it time evolves under the Hamiltonian (5.16). Thus, the coherence-loss process implied by Eqs. (5.10)–(5.13) can be attributed to the deviation of excitons from

ideal Bose behavior, i.e., to the kinematic and dynamical interactions.

VI. COHERENT OPTICAL EXPERIMENTS

In this section we describe within the quantum mechanical framework some typical coherence-loss experiments that have been traditionally understood within the statistical model, and outline a situation in which the quantum mechanical model could be verified experimentally.

In recent years, several techniques have been developed for following the time evolution of a coherent state. A general experiment can be considered as consisting of three steps involving (1) preparing the coherent state at $t = 0$, (2) allowing the system to time evolve for $0 < t < t_1$, and (3) probing the system at $t = t_1$ through a process that measures the excited state population or the coherent polarization. In many optical experiments, such as those developed for monitoring T_1 and T_2 relaxation in molecular vibrations,[20] the experimental observable is the intensity of a light signal. A longitudinal relaxation experiment often measures the intensity (as a function of the time t_1) of the omnidirectional signal which results from the spontaneous radiative interaction of the excited collection. According to Eq. (3.23), the intensity of this signal is proportional to the excited state population in the collection, and thus permits one to monitor the population decay by varying in successive experiments the time t_1. On the other hand, monitoring transverse relaxation can be accomplished by measuring the intensity (as a function of t_1) of the directional beam which originates from the interaction of the collective coherent state with the radiation field. Within the statistical model, the oscillating macroscopic polarization, the directional light intensity, and its optical spectrum are intimately related: The directionality and low divergence of the emerging beam are understood to indicate that it is a coherent emission; its intensity, then, is calculated from the absolute square of the electric-field amplitude, which in turn is proportional to the amplitude of the oscillating macroscopic polarization. The directional intensity is therefore at all times proportional to the square of the polarization, as in Eq. (3.22). The time evolution of the polarization can be written as

$$\text{tr}[\rho \sigma^-(t)] = \cos\frac{\theta}{2} \sin\frac{\theta}{2} \sum_{j=1}^{N} \langle 0|\sigma^-_j(t)\sigma^+_j|0\rangle \tag{6.1}$$

and thus corresponds to the Fourier transform of the absorption spectrum of the ensemble.

Measurements of T_1 and T_2 relaxation may be described in the quantum mechanical model as follows: A coherent state is created in a macroscopic sample by a directional laser beam of wave vector k. It is therefore described by a MUW having directional phase structure describable by a wave vector k, as in Eqs. (5.3) and (5.4). Emission of a photon of wave vector k' causes a downward transition in the collection. The final collective state after such an emission is obtained by applying the annihilation operator $R^-_{k'}$, [Eq. (5.1b)] to the initial state. The intensity of a light signal emitted

by the collection at time t in the direction k' is given by the probability of observing a photon of wave vector k' at t, which in turn is proportional to the probability that the collection can effect a downward transition at time t, characterized by a phase structure k'. For a collection initially in a coherent state $||\theta_k\rangle$ [Eq. (5.3)] it is

$$I_{\theta k}^{k'}(t) = \sum_{\alpha} |\langle\alpha|R_{-k'}^-||e^{-i\mathfrak{X}t}\theta_k\rangle|^2 , \qquad (6.2)$$

where the summation is over all possible final states. The states $|\alpha\rangle$ form a complete set and thus the summation may be carried out giving

$$I_{\theta k}^{k'}(t) = \langle\theta_k||e^{i\mathfrak{X}t}R_{k'}^+ \cdot R_{-k'}^- e^{-i\mathfrak{X}t}||\theta_k\rangle . \qquad (6.3)$$

When $k' = k$, the emission has the same direction as the phase structure of the coherent state, corresponding to the "directional signal" measured in transverse relaxation experiments, while $k' \neq k$ corresponds to the omnidirectional signal monitored in population decay measurements.

At $t = 0$, when the collective excitation is in a fully coherent state, the directional intensity is approximately equal to the square of the coherent amplitude (see Appendix A)

$$I_{\theta k}^{k}(0) = N(N-1)\sin^2(\theta/2)\cos^2(\theta/2) + N\sin^2(\theta/2) , \qquad (6.4)$$

while the omnidirectional intensity is proportional to the population

$$I_{\theta k}^{k'}(0) = N\sin^2(\theta/2) , \qquad (6.5)$$

as in the statistical model. An interaction which causes the loss of the minimum-uncertainty characteristics of the coherent wave packet by destroying coherence to all orders causes a decay of the intensity of the directional beam. This decay can be shown by calculating the emission probability in the direction k from an incoherent state of the form (4.11) resulting from such a coherence-loss process. The intensity of a light signal emitted by such a state is proportional to the mean number of excitations (calculated in Appendix B)

$$I_{\rho_z} = N\sin^2(\theta/2) \qquad (6.6)$$

and is independent of the direction of measurement, indicating that destruction of coherence to all orders (complete phase randomization) produces a complete loss of directionality in the emitted light. Finally, a process which causes the decay of population in the collection brings about the decay of both the directional and the omnidirectional signals, since it produces a decay of the quantity θ in Eqs. (6.4)–(6.6).

Therefore, both within the quantum mechanical and the statistical models, the intensity of the omnidirectional signal is at all times proportional to the population and thus can be used as a monitor for the longitudinal relaxation process. The time constant that is obtained if the decay is exponential corresponds to the phenomenological time constant T_1 of the statistical model. The decay of the directional signal gives the time evolution of the squared macroscopic polarization due to coherence relaxation to *all orders* within the quantum mechanical

model: The decay rate corresponds to the phenomenological constant $T_2/2$ of the statistical model.

An interaction which causes the decay of the coherent macroscopic polarization while preserving one or more orders of coherence of the MUW does *not* affect the time dependence of the two intensities, since the intensity in the direction k' from a first-order coherent state of the form (4.10) is given by an expression similar to Eq. (A11), i.e., both the directional and the omnidirectional signals display the same intensity as if the emitting state were fully coherent. Thus, in the presence of interactions which preserve first-order coherence, the directional intensity is *not* proportional to the squared polarization, contrary to the assertion of the statistical model. Moreover, the time dependence of the directional intensity is not the Fourier transform of the spectrum, since the correlation function

$$G^{(1)}(\tau, 0) = \langle\theta_k||R_k^+(\tau)R_{-k}^-||\theta_k\rangle \qquad (6.7)$$

contains contributions from all processes that cause the decay of the coherent polarization, including those that preserve first-order coherence. Because of the angular momentum properties of the collective operators, Eq. (6.7) is not proportional to the macroscopic polarization except under small amplitude conditions, where

$$G^{(1)}(\tau, 0) = \langle\beta_k||B_k^+(\tau)B_k||\beta_k\rangle = \beta\langle\beta_k||B_k^+(\tau)||\beta_k\rangle . \qquad (6.8)$$

In view of the above discussion, it is possible to test the validity of the quantum mechanical treatment of coherence in optical experiments by examining experimentally the relationship of the time dependence of the intensity of the directional beam emitted by the coherent state to the macroscopic polarization[21] and the Fourier transform of the spectrum of this emission. Within the statistical model these quantities are always proportional. Any lack of proportionality would indicate the presence of interactions which preserve coherence only to first order. A deviation from the conventional relationship between the intensity evolution and the Fourier transform of the spectrum underlines the importance of molecular correlations which are implicitly taken into account in the collective operators, and points to the inequivalence of Eqs. (6.1) and (6.7).

A system in which such experiments might be conducted is that of a molecular crystal. At low temperatures, exciton–phonon interactions may not contribute significantly in the time evolution of a coherent exciton wave packet and coherence loss is dominated by interactions resulting from the presence of disorder.[22] Such interactions can be described as mixing different q states[23] and thus destroy coherence to all orders. If the problem of disorder can be sufficiently overcome technically in the preparation of nearly perfect crystals (or if large-amplitude excitation of a crystal can be achieved), then it should be possible to observe the process of coherence loss due to dynamic and kinematic interactions among the excitons (as discussed in Sec. V A), thus making the effects of first-order coherence-preserving interactions accessible to experimental observation.

VII. SUMMARY

Optically prepared coherent states in matter are traditionally represented through a statistical model. The material system is regarded as a statistical ensemble of two-level molecules, and the coherent state consists of the in-phase excitation of all molecules into superpositions of their ground and excited states, so that the ensemble displays an oscillating macroscopic polarization. This model, however, is inapplicable in quantum mechanical situations such as those involving spontaneous emission or delocalized collective states, as in crystals.

It is possible to treat a collection of two-level molecules completely quantum mechanically through the formalism of collective operators and states. In this quantum mechanical treatment, the final state of a laser-driven molecular collection can be expressed as a minimum uncertainty wave packet composed of all the collective states accessible by the radiation field. Such a state exhibits all the features of the conventional statistical model for coherence: it displays a nonzero expectation value for the polarization operator, which oscillates sinusoidally with a definite phase; the in-phase and out-of-phase components of this expectation value, together with the expectation value of the population-difference operator, can be used to construct a vectorial model for the coherent state, completely equivalent to the pseudo-spin model conventionally used in the statistical treatment of coherence. At the same time, the quantum mechanical coherent state exhibits all the quantum mechanical features which are not included in the conventional statistical model: it can account for spontaneous emission from a coherent state, it can adequately describe coherence in the presence of delocalizing interactions, and it can be used to calculate the spectral properties of a collection of molecules through the two-time first-order correlation function. It reduces to the statistical description of a coherent state if quantum mechanical correlations among the molecules in the collection can be neglected.

Macroscopic collections of molecules interacting with light can be described through the formalism of phased collective operators and the corresponding states. A special case of this formalism can be used to describe molecular crystals, thus permitting the quantum mechanical treatment of coherent states in such systems. In the limit of low excitation densities within the small amplitude approximation, this formalism goes over smoothly to the usual molecular exciton theory.

The time evolution of a minimum-uncertainty wave packet in the interaction picture can be described as a population decay, or as a loss of its minimum uncertainty characteristics. These processes correspond to the longitudinal (T_1) and transverse (T_2) relaxations of the statistical model. Using the formalism of *orders of coherence* analogous to that of quantum optics, different types of T_2 processes can be distinguished for a minimum uncertainty wave packet, each one causing the decay of different orders of coherence of the wave packet. The quantum mechanical process which most closely corresponds to the phase randomization of the statistical model consists of the decay of all orders of coherence of the minimum uncertainty state. Transverse relaxation processes preserving one or more orders of coherence have no equivalent in the statistical model.

Experimentally, the time evolution of a coherent state is monitored through its interaction with the radiation. Population decay (T_1) is followed through the time dependence of the omnidirectional light signal emitted by the collection, while polarization decay (T_2) is studied through the time dependence of the directional coherent emission. Such experiments can be adequately described through the quantum mechanical formalism of collective operators and collective coherent states. The quantum mechanical interpretation of population decay experiments coincides with that of the statistical model. However, experiments monitoring T_2 relaxation are viewed differently in the two models: Within the quantum mechanical model, the time dependence of the directional intensity is not simply the decay of the coherent polarization, if interactions preserving first-order coherence are present. Also, the time evolution of the coherent polarization is not directly related to the spectrum of the emitted radiation when quantum mechanical correlations among molecules exist and the small-amplitude approximation is inapplicable. The quantum mechanical interpretation of such an experiment reduces to that of the statistical model if interactions preserving first-order coherence are absent and if the excitation density in the collection is low.

APPENDIX A: INTENSITY CALCULATIONS FOR FULLY COHERENT STATES

The probability of emission of a photon in the direction k' from a coherent excitation prepared by a laser beam of wave vector k is given by

$$I_{\theta k}^{k'} = \langle \theta_k || R_{k'}^+ \cdot R_{k'}^- || \theta_k \rangle . \tag{A1}$$

The phased creation/annihilation operators have the commutation properties

$$[R_{k'}^+, R_k^-] = \sum_{j,l} \exp[i(k'r_j + kr_l)] (\sigma_j^+, \sigma_l)$$

$$= 2 \sum_j \exp[i(k+k')r_j] \sigma_{zj}^+ \equiv 2R_{z(k+k')} \tag{A2}$$

and

$$[R_{zk}, R_{k'}^\pm] = \pm R_{k+k'}^\pm . \tag{A3}$$

The phased population difference operator R_{zk} acting on the ground state gives

$$R_{zk}|0\rangle = -\frac{1}{2} \sum_j e^{ikr_j}|0\rangle . \tag{A4}$$

Using Eqs. (A2)–(A4) we may obtain the emission probability in the direction k' for the state created by the absorption of n radiation quanta of wave vector k

$$I_{nk}^{k'} = \langle 0| (R_k^n) R_{k'}^+ \cdot R_{k'}^- \cdot (R_k^+)^n |0\rangle$$

$$= n! \, n \, \frac{(N-2)!}{(N-n)!} \left[(n-1)N + (N-n) \left| \sum_j \exp[i(k-k')r_j] \right|^2 \right] . \tag{A5}$$

For the case $k' = k$,

$$\sum_j \exp[i(k - k')r_j] = N ,$$ (A6)

so that the emission probability in the direction $k' = k$ from that state is

$$I^k_{nk} = \frac{n!\,N!}{(N-n)!}\, n(N-n+1) .$$ (A7)

For $k' \neq k$ the phase factor may be written as

$$\left| \sum_{j=1}^N \exp[i(k-k')r_j] \right|^2$$

$$= N + \sum_{j \neq l} \exp[i(k-k')(r_j - r_l)] .$$ (A8)

The last term has to be calculated explicitly, given the relative positions of all the molecules in the collection. However, for a collection of large dimensions, such that

$$\max(r_j - r_l)(k - k') \gg 1 ,$$ (A9)

this term can be taken equal to zero if the intermolecular distances are uniformly distributed. In such a case, the probability of emission of a photon of wave vector $k' \neq k$ satisfying Eq. (A9) is

$$I^{k'}_{nk} = \frac{n!\,N!}{(N-n)!}\, n .$$ (A10)

Using the definition of Eq. (4.3) for the coherent wave packet, we may rewrite Eq. (A1) as

$$I^{k'}_{\theta k} = \left(\cos^2 \frac{\theta}{2}\right)^N \sum_{n=0}^N \frac{\left(\tan^2 \frac{\theta}{2}\right)^n}{(n!)^2}\, I^{k'}_{nk} .$$ (A11)

Thus, the intensity emitted by a coherent excitation $||\theta_k\rangle$ in the direction k is

$$I^k_{\theta k} = N(N-1) \sin^2(\theta/2) \cos^2(\theta/2) + N \sin^2(\theta/2) ,$$ (A12)

while the emission along $k' \neq k$ is given by

$$I^{k'}_{\theta k} = N \sin^2(\theta/2) .$$ (A13)

APPENDIX B: INTENSITY CALCULATIONS FOR DEPHASED STATES

As discussed in Sec. IV, a state of the form (4.11) is the quantum mechanical analog of the state resulting from the dynamical phase randomization of a coherent excitation in an ensemble within the statistical model. Clearly, such a state cannot define a preferential direction characterized by a wave vector k, and thus its representation should be the same in all cooperation bases $\{r_k\}$. The emission intensity from such a state, therefore, is independent of the direction of measurement. It may be obtained as

$$I = \text{tr}\{\rho^{(2)} R^+ R^-\} = \left(\cos^2 \frac{\theta}{2}\right)^N \sum_n \left(\tan^2 \frac{\theta}{2}\right)^n$$

$$\times \sum_{r,\alpha} \langle \alpha, r, n | R^+ R^- | n, r, \alpha \rangle .$$ (B1)

From the formal analogy of R^+ with the angular momentum operators we have

$$\langle \alpha, r, n | R^+ R^- | n, r, \alpha \rangle = \left(n + r - \frac{N}{2}\right)\left(\frac{N}{2} + r - n + 1\right)$$ (B2)

independent of α. Since there are

$$g_r = \frac{N!\,(2r+1)}{\left(\frac{N}{2}+r+1\right)!\left(\frac{N}{2}-r\right)!}$$ (4.12a)

values of α for each r, the summation over r and α reduces to

$$\sum_{r,\alpha} \to N! \sum_{r=|N/2-n|}^{N/2} \frac{(2r+1)\left(n+r-\frac{N}{2}\right)\left(\frac{N}{2}+r-n+1\right)}{\left(\frac{N}{2}+r+1\right)!\left(\frac{N}{2}-r\right)!}$$

$$= \frac{N!}{(n-1)!\,(N-n)!} .$$ (B3)

This last equality may be proved by induction on $s = (N/2) - r$. The emission from a dephased state along any spatial direction, therefore, is

$$I_\rho(2) = \left(\cos^2 \frac{\theta}{2}\right)^N \sum_{n=0}^N \frac{N!}{(n-1)!\,(N-n)!} \left(\tan^2 \frac{\theta}{2}\right)^n$$

$$= N \sin^2 \frac{\theta}{2} .$$ (B4)

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ference experiments expressible through nth order n-time correlation functions (e.g., the Hanbury—Brown Twiss experiment for $n=2$). In material excitations, Eq. (4.9) implies that probability-interference experiments would give the same result whether a state is coherent or has lost its minimum uncertainty characteristics. Thus, coherence-loss processes could be monitored only through amplitude-interference experiments.

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