

Detecting quantum superpositions of classically distinguishable states of a molecule

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We present a method for the unambiguous detection of a classically distinguishable coherent superposition state in the vibrational coordinate of a diatomic molecule. The configuration of the state may be observed via the time-dependent spectrum of spontaneous emission from the molecule. The signature of the states in the emission spectra is discussed, as are the practical possibilities for experiments on a realistic molecular system.

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I. INTRODUCTION

Central to the interpretation of quantum mechanics is the question of the extent to which it is possible to prepare, maintain, and unambiguously detect a coherent superposition of classically distinguishable states. By classically distinguishable states we mean those that are well localized in a continuous coordinate-momentum phase space. Within this definition, systems with degrees of freedom that have no classical analog, such as spin systems or idealized two-level atoms, cannot exhibit such states.

A discussion of classically distinguishable coherent superposition states (or "superposition states" for short) is a necessary precursor to a discussion of the Schrödinger cat [1], the distinction being that the former may be discussed in the context of microscopic or mesoscopic systems, whereas the latter is reserved exclusively for macroscopic systems. A key feature of all these states is the coherence that exists between their well-localized and well-separated components [2], and it is this aspect that distinguishes them from a classical-like mixed state.

There are three important issues that must be addressed in any discussion of experiments for these states: their preparation, survival, and measurement. First, it is clear that a vital ingredient for any experiment is the availability of a system in which it is certainly possible to generate quantum coherence. This is not an obviously achievable objective for a truly macroscopic system. Second, the environment in which these states can exist for any length of time must be well isolated, since even small amounts of dissipation can destroy the superposition that is their hallmark. Finally, and equally important, is the availability of measurement apparatus that can distinguish unequivocally between the coherent superposition state and a classical mixture.

Schrödinger's original proposal [3–5] fails to meet any of the criteria of creation, isolation, and detection. The reason is that in a truly macroscopic system (by any measure) both preparation and sustenance of the state are inordinately difficult because it is impossible to isolate the

system sufficiently well. Furthermore, a single measurement on a single quantum system of this kind cannot reveal the state of that system. Thus it makes sense to examine an intermediate regime: a collection of noninteracting microscopic systems that nonetheless have a continuous degree of freedom, for which all three criteria are satisfied and in which there is the possibility of generating states that exhibit all the salient features of the cat state, excepting their macroscopic nature.

There has been much discussion of possible ways to generate versions of this class of superposition states in the electromagnetic radiation field via nonlinear optical processes [6,7]. The question of just how easily the characteristic coherences are destroyed by dissipation has thus been examined by several authors [8–10]. Much of the discussion is rendered hypothetical by the difficulty of generating and detecting optical superposition states. The difficulty arises because even the loss of a single photon destroys the visibility of the interference fringes in the photoelectron distribution that signify the quantum coherence of the superposition state. Consequently, the more well separated and thus "macroscopic" the components are, the more difficult it is to detect their underlying coherence.

An alternate system that allows much better isolation from the environment of the internal continuous degree of freedom has been proposed recently for the study of superposition states by several authors [11,12]. This system, the vibrational degree of freedom of a molecule, affords precise control over its configuration by optical excitation. Furthermore, the effects of dissipation (i.e., non-Hamiltonian evolution) are minimal over the time scale of many vibrational periods and thus it has a significant advantage over the proposed nonlinear optical schemes. Such a quantum-mechanical system is clearly not macroscopic by all measures. It does, however, enable all three criteria for the study of classically distinguishable coherent superposition states to be satisfied and thus provides a reasonable starting point for their experimental exploration.

The main point discussed in this paper is a method of

detecting these superposition states, and their signature in such measurements. Although this issue is a critical one, it has not received much attention in the literature and thus the detectability of superposition states in a matter system has not been properly addressed. We begin with a simple perturbation theory analysis of the generation of the states in terms of the eigenstates of the vibrational Hamiltonian. Although the results of this part of our analysis are the same as found by Janszky *et al.* [12], this view brings out explicitly the role of the Franck-Condon factors in determining the shape of the well-localized classical-like components of the state. We then use this state to calculate the time-dependent spectrum of spontaneous emission and examine the role of the experimental parameters in determining the shape of the spectrum. Finally, we assess the potential for experiments in a real homonuclear molecule.

II. GENERATION AND SURVIVAL

Consider the case of a diatomic molecule in which there is a single vibrational degree of freedom. Following irradiation of the molecule by a sequence of optical pulses, its wave function takes the form (in the limit of weak electric fields, with Rabi frequencies consistent with the Born-Oppenheimer approximation)

$$\Psi(q, \vec{x}, t) = \Psi_g(q, t)\phi_g(\vec{x}) + \Psi_e(q, t)\phi_e(\vec{x}), \quad (1)$$

where \vec{x} and q are the (vector) electronic and (scalar) nuclear coordinates and $\Psi_g(q, t)$ and $\Psi_e(q, t)$ are the nuclear wave functions in the ground and excited electronic states, respectively. $\phi_g(\vec{x})$ and $\phi_e(\vec{x})$ are the ground and excited electronic state wave functions after photoexcitation but before the molecule has undergone any spontaneous emission. Since we will propose a detection technique that is sensitive to the nuclear motion in the excited electronic state, we will ignore the part of the wave function in the ground electronic state. The relevant part of the nuclear wave function is

$$\Psi_e(q, t) = -i \frac{d_{eg}}{\hbar} \sum_{\nu'=0}^{\infty} \tilde{E}(\Delta - \omega_{\nu'}) W_{ge}^{(\nu', 0)} e^{-i\omega_{\nu'} t} \Psi_e^{(\nu')}(q), \quad (2)$$

where $\Psi_e^{(\nu')}(q)$ is the ν th vibrational eigenstate of the excited electronic state, with energy $\hbar\omega_{\nu'}$, and $\Delta = \omega_L - \omega_{eg}$ is the detuning of the pulse pair's mean frequency ω_L from the $(\nu''=0, \nu'=0)$ transition frequency ω_{eg} (ν'' labels the vibrational eigenstates of the ground electronic states). $W_{ge}^{(\nu', 0)}$ is the Franck-Condon factor connecting the $(\nu''=0, \nu')$ eigenstates of the nuclear degree of freedom and $\tilde{E}(\omega)$ is the spectrum of the (scalar) electric field of the exciting pulse sequence. d_{eg} is the dipole matrix element of the electronic transition, which is taken to be independent of the nuclear separation. If the potential in which the nuclei move is anharmonic, then a single pulse suffices to create a superposition state, by exactly the same mechanism as outlined by Milburn [13] and by Yurke and Stoler [6] for an optical field. This class of superposition states is transitory—they appear only for a short time near $t = 2\pi/\beta$ after excitation, where β is the anharmonicity of the spacing of the eigenstates of the

Hamiltonian. In the language of mechanical wave packets they occur during the times of the one-half fractional revivals [14] and to this extent may plausibly be claimed to have been observed by Yeazell, Mallalieu, and Stroud [15] in an atomic Rydberg electronic wave packet. Here we propose another scheme in which the superposition state is generated in a quasiharmonic region of the wave packet's motion in a controlled manner and is detected directly.

The important point to note is that in this weak-field approximation the phases of the nuclear eigenstates are set by the phase of the relevant spectral components of the optical field and thus appropriate manipulation of the optical phase can produce radically different nuclear states. It is this feature that plays a central role in the generation of the superposition states. Consider, for example, the action of a short pulse with electric field of the form $E(t) = f(t)e^{-i\omega_L t} + \text{c.c.}$ incident upon a sample of molecules whose nuclear vibrational potentials are harmonic. Suppose further that both potentials have the same harmonic frequency ω but have separated equilibria, the separation being characterized by κ , the ratio of the physical separation of equilibrium positions (D) to the spatial extent of the nuclear vibrational ground-state wave function $(\sqrt{2\hbar/m\omega})$, where m is the reduced mass. In this case the Franck-Condon factors linking the nuclear vibrational ground state of the ground electronic state to the various nuclear eigenstates of the excited electronic state nuclear Hamiltonian are

$$W_{ge}^{(\nu', 0)} = \frac{(-\kappa)^{\nu'} e^{-\kappa^2/2}}{\sqrt{\nu'!}}. \quad (3)$$

Then the populations of the nuclear eigenfunctions of the excited electronic states are Poisson distributed, with mean vibrational quantum number $\bar{\nu}' = \kappa^2$. Thus if the pulse is transform limited with an energy spectrum whose width $\delta\omega$ is much larger than the spectral range of the Franck-Condon factors (i.e., $\delta\omega \gg 2\omega\kappa^2$), then the molecule is excited in the quasi-impulsive limit and $f(t) \cong \delta(t)$. The nuclei in the excited electronic state of the molecule are left in a coherent state $\chi_{\kappa}(q, t)$ [1] with amplitude κ following the pulse. The coherent state is the most classical-like state of the harmonic oscillator [16], in which the wave packet executes simple harmonic motion while at all times remaining a minimum-uncertainty state. A suitable form of $f(t)$ also produces a coherent state in a molecule whose vibrational frequencies are different in the ground and excited electronic states [17].

In the case when the exciting radiation consists of a pulse pair, both of which satisfy the quasi-impulsive criterion, then the exciting field has the form

$$E(t) = \{f(t) + \alpha f(t - \tau_D)\} e^{-i\omega_L t} + \text{c.c.},$$

where τ_D is the delay between the two pulses and is taken to be fixed over the experimental ensemble to a fraction of an optical period, possibly in a manner similar to that used by Scherer *et al.* [18]. If $\alpha = 1$, then the (unnormalized) wave function describing the nuclear degree of freedom after photoexcitation is

$$\Psi_e(q, t) = \chi_\kappa(q, t) + e^{i\theta} \chi_\kappa(q, t - \tau_D), \quad (4)$$

where $\theta = \omega_{eg} \tau_D$. The excitation sequence produces a coherent superposition of two nuclear vibrational coherent states. The relative vibrational phase of the coherent state subpackets is determined by the delay of the two pulses in the exciting sequence compared to the vibrational period. If $\omega \tau_D = \pi$ then the nuclei are simultaneously localized at both inner and outer turning points of their periodic trajectories. Moreover, for $\kappa > 1$ this is an example of a *classically* distinguishable coherent superposition state as shown in Fig. 1, since the two subpackets are separated by a distance larger than the extent of each. Figure 1(a) shows the wave function of the state generated by the two-pulse sequence immediately following excitation, consisting of two coherent-state subpackets. The relative quantum phase of these components is determined by the delay of the generating pulse pair compared to the (optical) period of the electronic dipole transition and is therefore much more critical than the gross vibrational phase in terms of creating a superposition state. The coherence between the subpackets that is the distinguishing feature of a quantum as opposed to a classical superposition state is manifest at certain times during the nuclear evolution when the left- and the right-

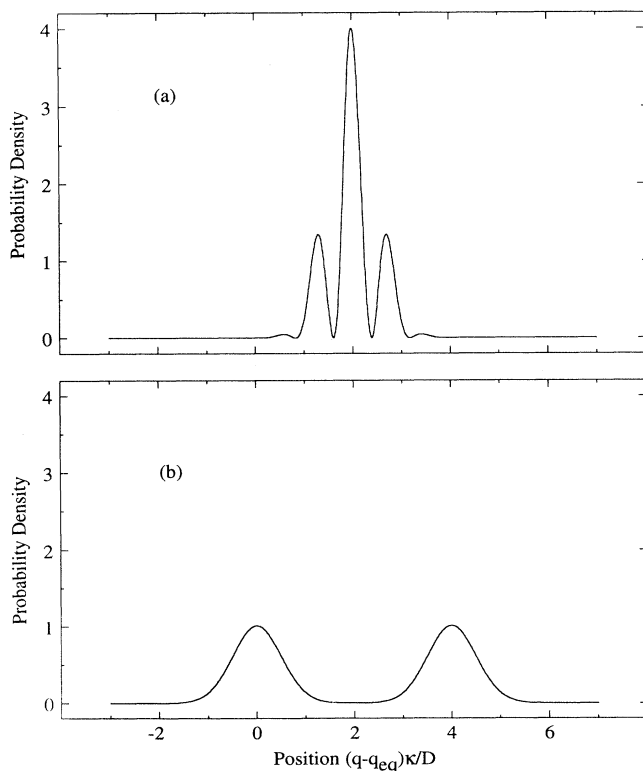


FIG. 1. Probability density for the internuclear separation of a superposition state in the vibrational degree of freedom of a harmonic molecule with $\kappa=2$ at different times t following excitation: (a) $\tau = \pi/2\omega$ and (b) $\tau = 2\pi/\omega$. The state is composed of two coherent-state vibrational wave packets and is created by the action of a pair of phase-locked short optical pulses separated by a delay $\tau_D = \pi/\omega$.

going wave packets collide near the potential minimum. At this juncture the wave function exhibits interference fringes, as shown in Fig. 1(b). The fringe spacing is related to the relative momentum of the two packets and this in turn is related to their initial separation 2κ . These molecular mechanical superposition states undergo purely Hamiltonian evolution for many periods before the coherence between the distinguishable subpackets is lost by vibrational dephasing due to intermolecular collisions. Moreover, the molecular vibrational mode Q factor is very high, on the order of 10^4 , so that it is possible to ignore the effects of dissipation completely during the initial evolution of the nuclear state. In fact, the vibrational motion of the molecule is by far the fastest dynamic occurring in this system. Other features that would preclude the generation of a coherent superposition state, such as molecular rotations or center-of-mass motion, are also insignificant on this time scale.

III. DETECTION

Detection of the superposition states in this mechanical system may be accomplished optically via the time-dependent spectrum of spontaneous emission from the excited electronic state of the system while the nuclei are in the wave-packet state. A system for measuring this has been demonstrated experimentally [19]. Janszky *et al.* propose, but do not analyze, another method whereby the excitation pulse is followed by a probe pulse that excites the system to one of two disjoint higher-lying levels, which they propose are detectable by a macroscopic apparatus. A similar analysis to that presented here may be performed for their setup and very similar conclusions result.

Consider the following simple model: a molecule with an electron in an excited state may at any time return to the ground state by the emission of a photon. The observed frequency of the photon will depend upon the separation of the nuclei at the instant of emission, since the electronic and nuclear degrees of freedom are coupled. Thus when the nuclear degree of freedom is in a wave-packet state, i.e., is well localized, and undergoes periodic evolution, the frequency of the emitted photons will likewise undergo a periodic modulation. The time-dependent spectrum of emission can be calculated using a physical model that is closely related to the actual experimental situation, along similar lines to those laid out by Eberly and Wodkiewicz [20,21]. The field radiated by the molecules as they decay is passed through a time gate that samples the field for a short duration T near a time τ after excitation of the molecule. The resulting temporal slice is then filtered through a spectrometer of passband γ and center frequency Ω and is incident upon an integrating photodetector. Thus, by varying τ and Ω a picture of the temporal evolution of the emission spectrum may be constructed. This method of detecting the wave packet projects out the dynamics of the nuclei in the excited electronic state of the molecule only [19]. This is an important feature of our detection scheme. It is only those molecules that are in the excited electronic state

that are also in the nuclear vibrational superposition state; those that remain unexcited electronically are not in a nuclear superposition state. Thus it is vital that the detection mechanism be able to select the appropriate subensemble of the molecules.

The resulting spectrum generated by the superposition state of Fig. 1, calculated using the methods described in Ref. [20], is shown in Fig. 2 for various times following excitation, for a time-gate duration of $\omega T = 1.0$ and spectrometer resolution $\gamma/\omega = 0.01$. Initially, and periodically thereafter, the well-localized and well-separated components of the superposition state are evident. One-quarter of a vibrational period after these times the two subpackets collide, giving rise to a modulation of the emission spectrum of about 10%.

A critical parameter in measuring such a spectrum is the duration of the time gate. If the gate is too short, the sampled spectrum will be a smeared-out version of the emitted spectrum and the fringes will be indistinct. If the gate is too long, then the wave packet will move during the time that the gate is open, again leading to a reduction of the fringe visibility. The choice of the optimum gate duration for detecting the superposition states is somewhat arbitrary. A reasonable rule of thumb that produces spectra with reasonable "fringes" and yet that correspond approximately to the wave-packet position

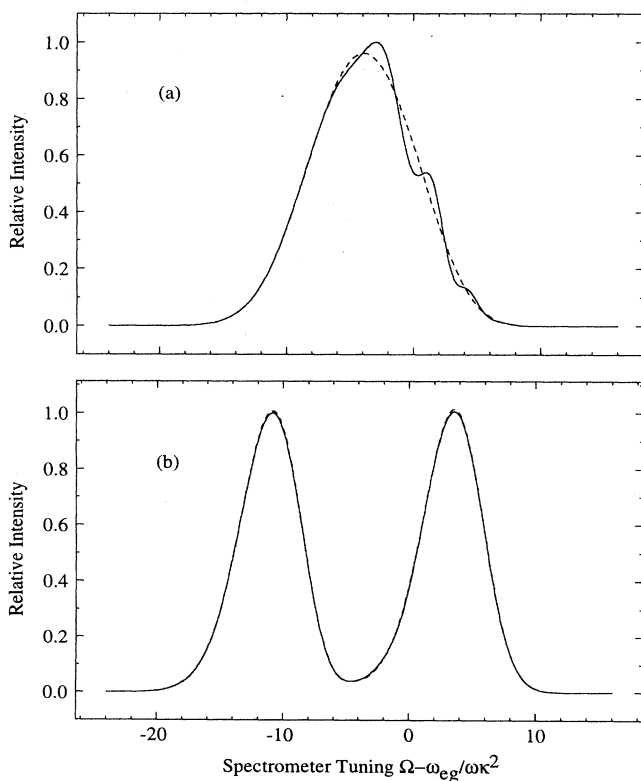


FIG. 2. Calculated spectrum of spontaneous emission from both the superposition state shown in Fig. 1 (solid lines) and the associated classical state (dashed lines). The spectra are for the same times after excitation as shown in Fig. 1. The time-gate duration is $T = 1/\omega$ and the spectrometer bandwidth is $\gamma = 0.01\omega$.

probability distribution at different times is that the gate duration satisfy $0.75 < \omega T < 1.5$, or a duration of about $1/(2\pi)$ times the vibrational period.

The most convincing manner in which to distinguish the spectral fringes arising from the superposition state is to measure the difference emission spectrum (DES), that is, the change in the emission spectrum when the two wave packets are coherently superposed compared to when they are not, normalized to the peak intensity, in other words, to measure the difference in the emission spectra of quantum and classical superpositions. Because the nuclear coherences are so intimately related to the optical coherence of the exciting pulse pair, it is straightforward to produce a classical mixture of the two wave packets by randomizing the relative optical phases of the generating pulse pair. The reduction of coherence may be accomplished rather simply; it only requires one to vary the relative delay between the pulses over the experimental ensemble over a range of one-half of an optical period. Alternately, a classical ensemble may be generated by randomly selecting one of the two exciting pulses before entering the medium, such that the experimental ensemble consists of 50% of each pulse in the pair. The calculated DES is shown in Fig. 3, using the same detection parameters as for the previous figures. Evidence of the coherent superposition is clearly seen.

The constraints imposed by the measurement of the superposition state by time-resolved spectroscopy set limits on the degree to which *macroscopic* coherent superposition state (i.e., those for which each of the subpackets has a mean vibrational quantum number $\bar{\nu}'$ very much greater than unity) may be observed. As $\bar{\nu}'$ increases, the interference fringes in the wave function have a progressively shorter scale length because of the increase in the relative momentum of the two colliding subpackets. As a consequence, it becomes increasingly difficult to detect the fringes in the DES. A detection signal-to-noise ratio of about 20 dB would limit $\bar{\nu}'$ to about 12.

This issue is also critical in applying the technique of molecular emission tomography [22] to the state in order

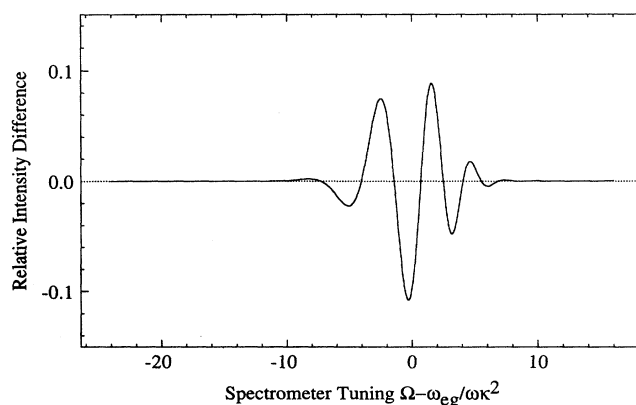


FIG. 3. Calculated difference emission spectrum for the superposition and classical state spectra shown in Fig. 2, at one-quarter period after excitation of the states. Evidence of the coherent superposition is clearly seen in the oscillations of the spectral intensity.

to reconstruct its density matrix. The problem arises because for tomographic reconstruction of a phase-space distribution from the emission spectrum to be effective it is necessary to use a gate pulse of duration much shorter than the vibrational period, so that the wave-packet dynamics are essentially frozen. This constrains the minimum bandwidth of each of the spectra, however, so that spectrally fine fringes have their visibility significantly diminished. This means that it is possible to reconstruct only a phase-space distribution in which the fringes that reflect the coherence between the localized components of the state are strongly diminished in amplitude as compared to fringes occurring in the Wigner distribution. If the full quantum wave function is not required, however, then the parameters specified in the previous paragraphs are adequate for detecting the presence of a superposition state unambiguously.

Practically the major difficulty in detecting the state arises in obtaining a fast time gate for the molecular fluorescence. For a sodium dimer in its ground electronic and nuclear states for example, the classically distinguishable state may be generated in the $A\ ^1\Sigma_u^+$ state by means of a pair 30-fs-duration pulses, delayed from one another by 150 fs, and with mean wavelength near 630 nm. A suitable time gate may be constructed using nonlinear optical techniques, such as sum- or difference-frequency mixing of the fluorescence with a short duration optical pulse in a nonlinear optical crystal. The optimum gate duration is about one-sixth of the vibrational period, or approximately 50 fs. A gating pulse of similar wavelength as the pump pulse will up-convert the emission near 725–342 nm. A spectrometer with a 0.5-nm passband provides the appropriate spectral resolution and the up-converted fluorescence is detected using a photon-counting apparatus [23]. Near this spectral region the DES (calculated using realistic nuclear vibrational wave functions for Na_2) exhibits modulations that are characteristic of the coherences between the state's localized components and have a spectral period of some

5 nm [24].

In principle it is also possible to examine the effects of intermolecular collisions on the coherence by watching the state over a time long compared to the average time between collisions. In a real gas-phase molecule this may be impractical, however, for two reasons. First, typical diatomic vibrational periods are in the vicinity of 300 fs, whereas typical collision times are on the order of nanoseconds. It is this feature that allows us to ignore dissipation in the dynamics of the wave packet. Second, most nuclear potentials are anharmonic and this causes the “decay” of the wave packet (at least in the restricted sense of its becoming delocalized) on a time of a few picoseconds, so that the initial superposition state does not persist for a time comparable to the collisional dephasing time. However, it may be possible to destroy the coherence by illuminating the molecules with intense infrared radiation that interacts with the internuclear quadrupole moment and thus to reduce the decoherence time to only a few vibrational periods.

The generation of classically distinguishable coherent superposition states is central to a number of significant questions concerning both the interpretation of the wave function and the quantum measurement process. Molecular nuclear vibrational wave-packet spectroscopy provides a means to create such states and to detect them in a straightforward and controlled manner and thereby opens the door to a number of fundamental experiments. Success in this regime might motivate a search to find systems in which such states could be robustly detected in the limit of large quantum numbers—this would begin to approach a true Schrödinger cat state.

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