

High-Resolution Spectroscopy Based on Atomic Coherences [and Discussion]

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High-resolution spectroscopy based on atomic coherences

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The paper surveys the techniques of Doppler-free spectroscopy based on the creation and detection of Hertzian coherence in atomic and molecular systems. The preparation of individual atoms in a coherent superposition of states with the use of broad-band optical excitation is discussed, with particular reference to excitation by pulsed tunable dye lasers. Time-resolved observations of the fluorescent light emitted by these atoms reveal the interference phenomenon known as quantum beats and enable Landé g -factors, fine and hyperfine splittings of excited levels to be determined. An account of progress in recent experiments with probe-beam monitoring and pulse trains from mode-locked dye lasers completes this review.

1. INTRODUCTION

A review of the recent literature on high-resolution atomic spectroscopy, such as might be made by a young graduate student starting research in this field, might lead him to believe that it was essential for him to have access to a tunable, single-frequency, continuous-wave (c.w.) dye laser together with its associated electronics and optics for active stabilization and frequency measurement. However, well before the invention of the tunable dye laser in 1967, the techniques of optical double resonance and optical pumping using broad-band, incoherent light sources had already produced a large volume of Doppler-free spectroscopic measurements. This early work is detailed in excellent reviews by zu Putlitz (1964), Budick (1967), Cohen-Tannoudji & Kastler (1966) and Happer (1972).

Valuable additional results for lifetimes, and for fine and hyperfine structure splittings, had been obtained by other Doppler-free techniques, namely the zero-field and high-field level-crossing methods, which make use of Hertzian coherence created in the atoms by broad-band optical excitation. Indeed, the zero-field level crossing or Hanle effect can justly claim to be the first Doppler-free spectroscopic method (Hanle 1924).

In the 1960s two further Doppler-free techniques based on atomic coherences were demonstrated, namely transient quantum beats induced by short pulse excitation and c.w. quantum beats induced by amplitude-modulated excitation. In recent years transient quantum beats induced by broad-band, pulsed dye lasers or by foil excitation of fast ion beams have been the subject of intensive effort. It is the intention of this review to recall the principles of this method and some of the early experiments in this field. I shall then illustrate the rapid progress that has been made in the last decade, further details of which are contained in the review articles by Haroche (1976), Happer & Gupta (1978), Dodd & Series (1978) and Andrä (1978). Finally I shall touch on extensions of the quantum beat method that use pulse trains from mode-locked lasers.

2. ATOMIC COHERENCE

(a) *The ensemble density matrix*

In experiments in atomic physics we are usually forced by the low sensitivity of detectors to investigate the properties of a sample containing N atoms, where N is usually a large number. The observable properties of this sample are then given in terms of the average values of physical observables, e.g. an operator \mathcal{M} , taken over the ensemble of independent atoms:

$$\langle \mathcal{M} \rangle = \frac{1}{N} \sum_{i=1}^N \langle \Psi_i | \mathcal{M} | \Psi_i \rangle. \quad (1)$$

If we use the most general description of the wavefunction of the i th atom in the sample, we know that this requires a linear superposition of energy eigenfunctions $|m\rangle$ with time-dependent coefficients:

$$\Psi_i(t) = \sum_m a_m^{(i)}(t) |m\rangle. \quad (2)$$

Substituting into (1) we find that

$$\langle \mathcal{M} \rangle = \frac{1}{N} \sum_{i=1}^N \sum_{m, m'} \rho_{mm'}^{(i)} \langle m' | \mathcal{M} | m \rangle, \quad (3)$$

where

$$\rho_{mm'}^{(i)} = a_m^{(i)}(t) a_{m'}^{(i)*}(t). \quad (4)$$

We can now define the matrix elements of the density operator ρ by the equation

$$\begin{aligned} \rho_{mm'} &= \langle m | \rho | m' \rangle = \frac{1}{N} \sum_{i=1}^N \langle m | \Psi_i \rangle \langle \Psi_i | m' \rangle \\ &= \frac{1}{N} \sum_{i=1}^N \rho_{mm'}^{(i)} \end{aligned} \quad (5)$$

and express the mean value of the observable \mathcal{M} by

$$\langle \mathcal{M} \rangle = \sum_{m, m'} \langle m | \rho | m' \rangle \langle m' | \mathcal{M} | m \rangle = \text{tr}(\rho \mathcal{M}). \quad (6)$$

(b) *Diagonal elements of the density matrix*

Although the density matrix is less familiar than a description of the system in terms of atomic wavefunctions, it does have the advantage that its elements have immediate physical significance. For instance, the probability of finding an atom of the vapour in the excited state $|m\rangle$ is given by ρ_{mm} . If $|\mu\rangle$ is introduced to represent sublevels of the ground state or of a state of lower energy, then familiar quantities such as the absorption coefficient, $\kappa(\omega)$, which depend on population differences, have forms such as

$$\kappa(\omega) = \frac{\pi e^2}{2\epsilon_0 m c} g_i f_{ik} \mathcal{N} (\rho_{\mu\mu} - \rho_{mm}) g(\omega), \quad (7)$$

where $g(\omega)$ is a normalized line-shape function and \mathcal{N} is the atomic number density.

Thus, conventional emission and absorption methods monitor only the diagonal components of the density matrix. This statement applies also to the more recently developed techniques of saturated absorption and two-photon absorption spectroscopy.

(c) Hertzian coherence and off-diagonal elements of the density matrix

In most of the experiments that I shall discuss in §3 the atoms are excited by broad-band light sources with very limited temporal coherence and the atoms are monitored by detecting fluorescent light emitted in an arbitrary direction. In these experiments we can therefore neglect the off-diagonal elements of the density matrix of the form $\rho_{\mu\nu}$, and the density matrix then reduces to a ground-state part ρ_g and an excited state part ρ_e . Since we are chiefly interested in the time development of ρ_e we may assume for the sake of simplicity that ρ_g has only diagonal elements, $\rho_{\mu\mu}$.

The off-diagonal elements of the excited-state density matrix for the i th atom, $\rho_{mm'}^{(i)}$, are complex numbers whose phases ϕ_i are determined by those of the wavefunction amplitude coefficients $a_m^{(i)}$ and $a_{m'}^{(i)}$, as shown by (4). When the average is performed over N atoms in (5) to determine the density matrix element, $\rho_{mm'}$, for the ensemble, two different physical situations may be distinguished.

The first situation arises when the ensemble of atoms is prepared in a random way so that all values of the phase ϕ_i are equally probable. This is the most common situation and, when N is sufficiently large, it ensures that the off-diagonal elements, $\rho_{mm'}$, of the ensemble density matrix are identically zero.

The second situation arises when the distribution of phases is not isotropic and the off-diagonal elements of the ensemble density matrix ρ_e are finite, $\rho_{mm'} \neq 0$. We then say that the ensemble of atoms possesses finite radiofrequency or Hertzian coherences. The reason for this terminology is that the off-diagonal elements $\rho_{mm'}$ have an associated time-dependence given by $\exp\{-i(E_m - E_{m'})t/\hbar\}$, as will be shown below. Since we are concerned with situations in which $|m\rangle$ and $|m'\rangle$ are magnetic states, (J, M_J) or (F, M_F) , of the same electronic term (nLS), the angular frequency $\omega_{mm'} = (E_m - E_{m'})/\hbar$ will lie in the radiofrequency band.

(d) Creation of Hertzian coherence

The most efficient method of preparing an ensemble of atoms with finite Hertzian coherence is to use optical excitation with polarized light. If the source of radiation has a short coherence time τ_c then the excitation is effectively instantaneous and may be described in terms of a rate process represented by the matrix A . In this case the rate at which the off-diagonal elements of the excited-state density matrix are created is given by

$$A_{mm'} = \frac{\pi U(\omega)}{\epsilon_0 \hbar^2} \sum_{\mu} \langle m | \hat{\boldsymbol{e}} \cdot \boldsymbol{D} | \mu \rangle \langle \mu | \hat{\boldsymbol{e}}^* \cdot \boldsymbol{D} | m' \rangle \rho_{\mu\mu} \quad (8)$$

where $U(\omega)$ represents the energy density of the incident radiation at the optical frequency $\omega/2\pi$, $\boldsymbol{D} = -\sum_{j=1}^n e \boldsymbol{r}_j$ is the electric dipole operator for the atom, and $\hat{\boldsymbol{e}}$ is the polarization vector describing the incident radiation. This expression may be simplified by defining an excitation matrix $F_{mm'}$ by

$$F_{mm'} = \langle m | \hat{\boldsymbol{e}} \cdot \boldsymbol{D} | \mu \rangle \langle \mu | \hat{\boldsymbol{e}}^* \cdot \boldsymbol{D} | m' \rangle \quad (9)$$

and we see that $A_{mm'}$ will be zero unless $\Delta m = |m - m'| \leq 2$.

When $|m\rangle$ and $|m'\rangle$ are Zeeman states of the same fine or hyperfine level, Hertzian coherence can be generated only when the polarization vector $\hat{\boldsymbol{e}}$ contains a coherent mixture of orthogonal polarization components, $\hat{\boldsymbol{e}}_q$, ($q = 0, \pm 1$) where $\hat{\boldsymbol{e}}_0$ coincides with the atomic quantization

axis. This ensures that the atoms are excited to a coherent superposition of different Zeeman states. However, for Hertzian coherence involving different fine or hyperfine levels this restriction does not usually apply.

(e) *Evolution of the excited atoms*

The differential equation which controls the time-development of the density matrix is known as the Liouville equation. It may be easily derived from the time-dependent Schrödinger equation and in operator form it is written as

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} [\mathcal{H}, \rho] - \Gamma \rho + \Lambda. \quad (10)$$

In this equation \mathcal{H} is the effective Hamiltonian operator that describes the fine and hyperfine structure and magnetic Zeeman splitting of an atom with nuclear spin I excited to a given electronic term (nLS); Λ is the matrix describing the excitation process, and $\Gamma = \sum_l A_{kl}$ is the total rate for the decay of the excited level by the spontaneous emission of radiation. In this review I shall ignore the contributions to the relaxation of the excited-state density matrix made by the effects of interatomic collisions and by trapping of the fluorescent light. These difficulties can be avoided experimentally by working at low atomic density or by using atomic beams.

Making use of the fact that the states $|m\rangle$ and $|m'\rangle$ are energy eigenfunctions, the time evolution of the Hertzian coherence $\rho_{mm'}$ is given by

$$\partial \rho_{mm'} / \partial t + (i\omega_{mm'} + \Gamma) \rho_{mm'} = \Lambda_{mm'}. \quad (11)$$

Spectroscopic techniques, based on Hertzian coherences, are made possible because of the characteristic angular frequency $\omega_{mm'}$ appearing in the second term of (11).

(f) *Fluorescent light emitted by polarized excited atoms*

In these techniques the evolution of the Hertzian coherence of the excited atoms is usually monitored by measuring the intensity of fluorescent light, having polarization vector \hat{e}' , which is emitted into the solid angle $d\Omega$ about a direction \hat{r} with polar co-ordinates (θ, ϕ) . For an atom excited to the pure substate $|m\rangle$ and decaying to a single lower-level substate $|\mu'\rangle$ the light intensity would be given by

$$\frac{dI}{d\Omega} = \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3} |\langle m | \hat{e}' \cdot \mathbf{D} | \mu' \rangle|^2, \quad (12)$$

when measured in photons per second per steradian. However, this result must be generalized for an ensemble of atoms in a coherent superposition of excited substates by defining the fluorescent light-monitoring operator L_F given by

$$L_F = \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3} \sum_{\mu} \hat{e}' \cdot \mathbf{D} |\mu'\rangle \langle \mu' | \hat{e}'^* \cdot \mathbf{D}. \quad (13)$$

The intensity of the fluorescent light observed is then obtained by applying (6), giving

$$dI/d\Omega = \text{tr}(\rho L_F). \quad (14)$$

3. TRANSIENT QUANTUM BEAT SPECTROSCOPY OF ATOMS

(a) Principles of transient quantum beat spectroscopy

I turn now to the first of two experimental methods that enable the evolution in time of the Hertzian atomic coherences to be studied, namely the transient quantum beat method. We assume that the atoms in the sample are excited by a short pulse, centred at time t_0 , from a source of optical radiation, such as a conventional spectral lamp or a pulsed tunable dye laser, whose spectral bandwidth $\Delta\omega$ is much greater than the Fourier transform-limited bandwidth set by the pulse duration Δt , i.e. we require $\Delta\omega \gg 1/\Delta t$. If, in addition, the pulse duration satisfies the following conditions:

- (i) $1/\Delta t \gg \Gamma$ (we may neglect decay during the excitation pulse duration);
- (ii) $1/\Delta t \gg \omega_{mm'}$ (we may neglect precession of the coherences during the pulse duration);
- (iii) $\Delta\omega \gg \omega_{mm'}$ (the spectral bandwidth encompasses all the excited states);

then (11) shows that the off-diagonal elements of the excited state density matrix evolve as

$$\begin{aligned} \rho_{mm'}(t) &= \rho_{mm'}(t_0) \exp\{-(\Gamma + i\omega_{mm'})(t - t_0)\} \\ &= \frac{U(\omega)\pi}{\epsilon_0 \hbar^2} \sum_{\mu} F_{mm'} \rho_{\mu\mu} \exp\{-(\Gamma + i\omega_{mm'})(t - t_0)\}. \end{aligned} \quad (15)$$

Applying the monitoring operator L_F , we obtain an expression for the intensity of fluorescent light observed after the pulsed excitation:

$$\frac{dI}{d\Omega} = \frac{U(\omega)}{8\pi\epsilon_0^2} \left(\frac{\omega}{\hbar c}\right)^3 \sum_{\substack{mm' \\ \mu\mu'}} F_{mm'} G_{m'm} \rho_{\mu\mu} \exp\{-(\Gamma + i\omega_{mm'})(t - t_0)\}, \quad (16)$$

where the emission matrix $G_{m'm}$ is defined by

$$G_{m'm} = \langle m' | \hat{\mathbf{e}}' \cdot \mathbf{D} | \mu' \rangle \langle \mu' | \hat{\mathbf{e}} \cdot \mathbf{D} | m \rangle. \quad (17)$$

Equation (16) contains terms that lead to a damped modulation of the intensity of the fluorescent light at frequencies corresponding to the energy separations between Zeeman sublevels or to separations between atomic fine or hyperfine structure states.

It is clear from (15) and (16) that these light beats after pulsed excitation are associated with the time evolution of the off-diagonal elements of the excited-state density matrix. They may be detected by time-resolved observations after pulsed excitation provided that the necessary Hertzian coherence has been created at time t_0 by excitation with polarized light. For an intuitive understanding of the origin of the beats in Zeeman sublevels, it is useful to note that light that is coherently polarized possesses a finite component of angular momentum at right-angles to the axis of quantization and that this transverse angular momentum is transferred to the atoms at the instant of excitation, thus creating finite values for the transverse components of the magnetic dipole moments, $\langle M_x \rangle$ and $\langle M_y \rangle$. The modulation of the fluorescent light may therefore be ascribed to the precession or evolution of these transverse magnetic moments about the axis of quantization, in a similar manner to the modulation of light seen by a stationary observer when a beam from a lighthouse periodically scans across his field of view.

In the general case, the phenomenon is best described as the result of a quantum-mechanical interference between the scattering amplitudes for the two or more possible, but in principle indistinguishable, routes which connect the initial state of an atom, $|\mu\rangle$, to its final state, $|\mu'\rangle$.

This approach should make it clear that these quantum beats could in principle be detected by observing light scattered from a single atom and are not the result of interference in the radiation scattered from many different atoms.

A major advantage of the transient quantum beat method is the fact that the atoms evolve freely and are not subjected to time-dependent external perturbations, such as an r.f. magnetic field. Thus although considerable experimental sophistication may be necessary to resolve accurately the time-dependent variation of the emitted intensity, the interpretation of the data once obtained is relatively simple. This, combined with important advances in the methods of excitation and signal processing, has turned what was initially merely an interesting but relatively unknown phenomenon into a major experimental technique in the field of atomic spectroscopy. In the last 15 years transient quantum beat spectroscopy has produced a wealth of measurements of atomic lifetimes, Landé g -factors, and fine and hyperfine structure constants.

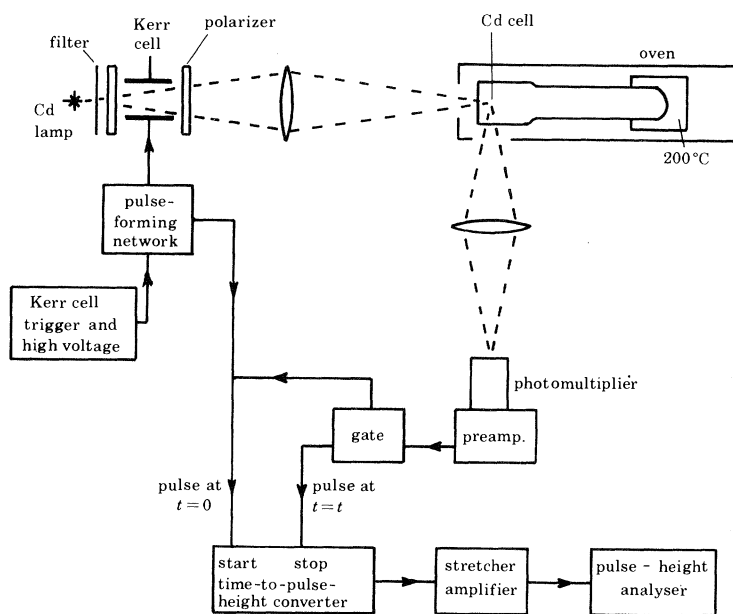


FIGURE 1. Block diagram of the apparatus used by Dodd *et al.* (1967) in resonance fluorescence experiments on cadmium vapour with the use of pulsed excitation.

(b) *Early observations of transient quantum beats*

The first observations of transient quantum beats were performed simultaneously by Dodd *et al.* (1964) and Aleksandrov (1964). The improved apparatus used by Dodd *et al.* (1967) in a more detailed study of the phenomenon is shown in figure 1. Zeeman quantum beats in cadmium vapour excited by the intercombination line $5^1S_0-5^3P_1$ at 3261 \AA † was chosen for this investigation. Cadmium atoms in a heated resonance cell were excited to the 5^3P_1 level by a pulse of resonance radiation lasting $0.2 \mu\text{s}$. This excitation pulse was obtained by passing the light from a commercial cadmium lamp through a Kerr-cell shutter operated by a high-voltage pulse unit. The time-dependence of the resonance fluorescence emitted in a

† $1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-1} \text{ nm}$.

direction perpendicular to both the direction of the incident light and a magnetic field applied to the atoms was recorded by using single-photon counting techniques.

The results obtained from a run with the cadmium vapour at 200 °C and an applied magnetic field of 34.5 μT is shown in figure 2*a*. This displays the number of events recorded on each channel of the pulse-height analyser after a correction has been made for the background count produced by photomultiplier dark current and by light reflected from the cell walls. The experimental trace can clearly be resolved into two distinct contributions, namely a

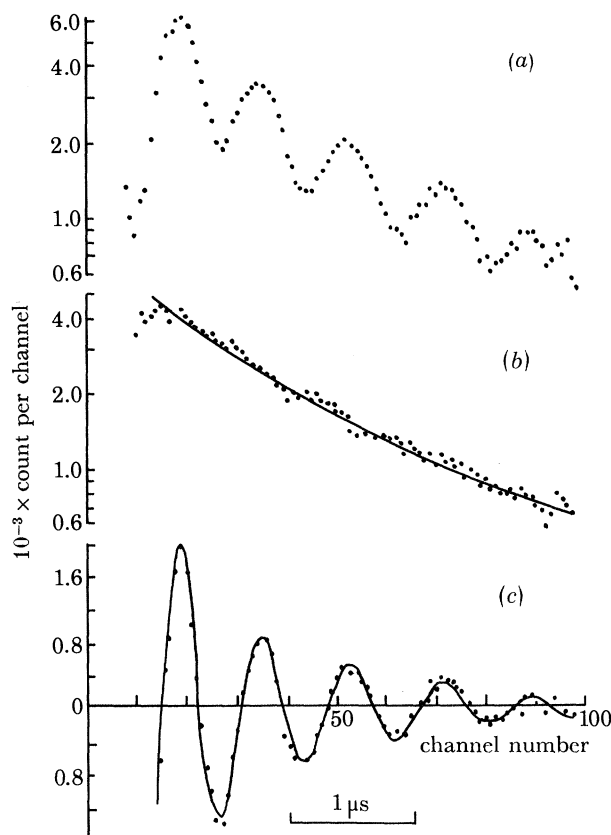


FIGURE 2. Transient decay of cadmium atoms excited by a pulse of polarized resonance radiation. (a) The experimentally observed fluorescence as a function of time. (b) The exponential decay of unmodulated fluorescent light. (c) The modulated component of the fluorescent light. The modulation is produced by Larmor precession in an applied magnetic field of 34.5 μT (after Dodd *et al.* 1967).

decaying but unmodulated intensity and a damped intensity modulation, shown in figure 2*b* and *c* respectively. The observed angular frequency of modulation $(9.25 \pm 0.30) \times 10^6 \text{ s}^{-1}$, at twice the Larmor frequency, is in good agreement with that calculated from the measured Landé g_J -factor for the 5^3P_1 level.

One of the principal difficulties connected with these early time-resolved experiments was the low intensity of conventional sources of pulsed radiation, a point emphasized by the fact that the signal shown in figure 2 required 7 h of data collection. In addition, the extension of the method to the detection of quantum beats at higher frequencies was constrained by the difficulty of obtaining fast optical shutters with large numerical apertures.

Fortunately, both these difficulties may be overcome by using pulsed, tunable dye lasers for optical excitation. Following an initial demonstration of the potential of these lasers by Gornik *et al.* (1972), the technique of transient quantum beats underwent a very rapid development and has been reviewed in detail by Haroche (1976). I proceed now to give a brief account of three investigations that have made use of this technique.

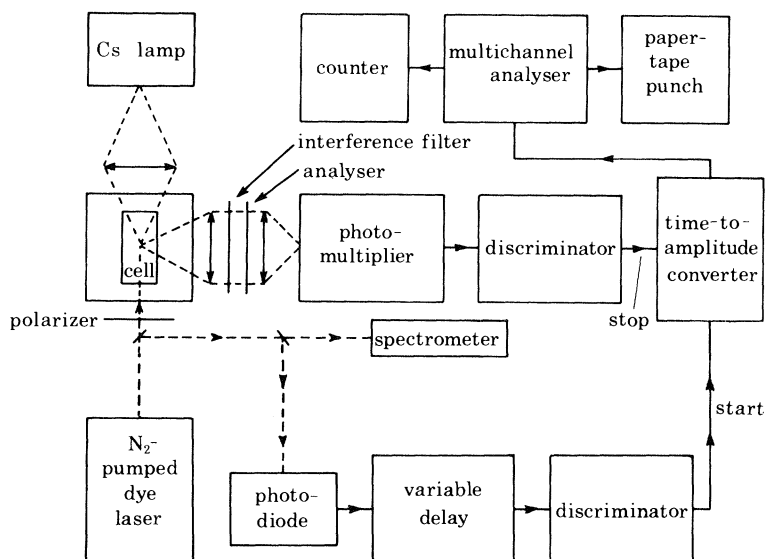


FIGURE 3. Arrangement of the apparatus used by Deech *et al.* (1975).

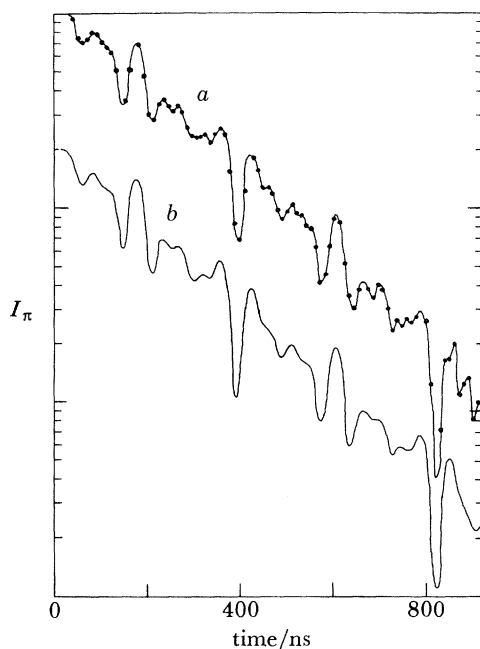


FIGURE 4. (a) Experimental quantum beat signal for $9\ ^2D_{3/2}$ level of caesium observed in π -polarized fluorescent light. (b) Theoretical curve calculated by using experimental values of $A(^2D_{3/2})$ and T (after Deech *et al.* 1975).

(c) *Transient quantum beat spectroscopy with pulsed laser excitation*(i) *Hyperfine structure measurements in caesium*

One of the first detailed investigations by this technique was made by members of Series's group at Reading and resulted in measurements of hyperfine structure, lifetimes and collisional relaxation of moderately high-lying 2S and 2D states in atomic caesium, ^{133}Cs . Fluorescence from these levels was generated by means of stepwise excitation. The first step, $6\ ^2S_{1/2} \rightarrow 6\ ^2P_{1/2,3/2}$ was accomplished by illuminating the vapour with resonance radiation from a conventional caesium lamp, and the second step from $6\ ^2P_{1/2,3/2}$ to higher 2S or 2D levels was induced by excitation with a nitrogen laser-pumped, pulsed tunable dye laser. The fluorescence was studied by single-photon delayed coincidence by using the apparatus shown in figure 3. By placing a linear analyser either parallel to or perpendicular to the polarizer in the laser beam, quantum beats could be detected corresponding to the hyperfine intervals $|\Delta F| = 1$ or $|\Delta F| = 2$ in zero field. A typical experimental record obtained by monitoring the fluorescence from the $9\ ^2D_{3/2}$ level is shown in figure 4.

Because the electric quadrupole interaction in ^{133}Cs is small compared with the magnetic dipole interaction, the hyperfine interval rule is obeyed to a good approximation. Thus the beat patterns represent the superposition of a relatively small number of terms with rationally related frequencies, and from a simple measurement of the period of the repeating pattern the reciprocal of the hyperfine interaction constant, $1/A(^2D_{3/2})$, could be determined with an accuracy of 1 part in 200. Detailed results for the $n\ ^2D_{3/2}$ levels with $n = 8$ to $n = 16$ are given in the publications by Deech *et al.* (1975, 1977) and Nakayama *et al.* (1981).

The experimental arrangement used by the Reading group has two obvious disadvantages: first, the population of atoms created in the $6\ ^2P$ levels by excitation with a conventional lamp is very small; and secondly the detection system is inefficient in that it can detect at best a maximum of one photon in each excitation and decay cycle. Both of these difficulties were overcome in the arrangement used by Haroche's group in Paris in quantum beat experiments in sodium.

(ii) *Fine structure measurements in sodium*

In the experiments reported by Haroche *et al.* (1974) and Fabre *et al.* (1975), stepwise excitation with two pulsed dye lasers was employed. The first laser pulse was tuned to the $3\ ^2S_{1/2} \rightarrow 3\ ^2P_{3/2}$ sodium resonance line at $5890\ \text{\AA}$, thus creating a large population in the $3\ ^2P_{3/2}$ level. The second laser was tuned to one of the $3\ ^2P_{3/2} \rightarrow n\ ^2D$ transitions and promoted atoms to a coherent superposition of the $n\ ^2D_{3/2,5/2}$ fine structure states. Fluorescent light emitted in transitions back to the $3\ ^2P_{3/2}$ level was detected and a complete record of the fine structure quantum beat pattern was recorded on each shot by using a Tektronix R7912 transient digitizer. The results of a large number of excitation and decay cycles were accumulated in the memory of a signal averager, and Fourier analysis of the beat pattern gave the fine-structure interval for the $n\ ^2D_{3/2,5/2}$ levels to an accuracy of about $\pm 1\ \text{MHz}$.

The efficiency of this experimental arrangement enabled a satisfactory record to be obtained for the $n = 9$ level at a $5\ \text{Hz}$ pulse repetition frequency in about 3 min. However, as the principal quantum number of the levels studied was increased, the number of pulses required to obtain a record with an acceptable signal:noise ratio also increased, changing from 1000 at $n = 9$ to 8000 at $n = 16$. This difficulty arises from the fact that the spontaneous transition

probability, A_{n3} , for the decay to the $3^2P_{3/2}$ level effectively involves an overlap integral of the n^2D and 3^2P wavefunctions. This decreases rapidly as n increases and makes the detection of quantum beats from high Rydberg levels by fluorescence monitoring almost impossible.

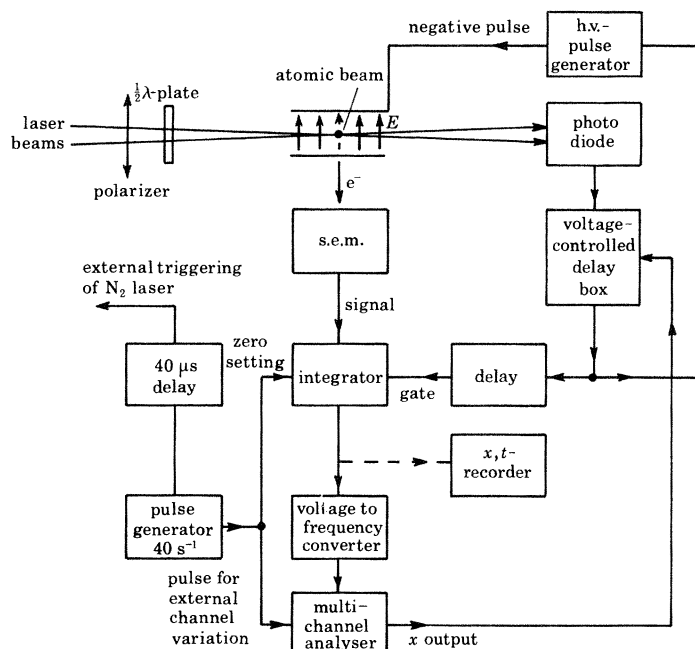


FIGURE 5. Schematic of the experimental arrangement used by Leuchs & Walther (1979).

Fortunately quantum beats in Rydberg levels can be monitored by using the field ionization detection technique, as Leuchs & Walther (1979) have recently demonstrated with the apparatus shown in figure 5. In these experiments sodium Rydberg levels with $n = 21$ to $n = 31$ were again populated by stepwise excitation by two tunable dye lasers pumped by the same pulsed nitrogen laser. However, to eliminate the effect of collisions, the sodium atoms were in the form of an atomic beam. Rydberg atoms were sampled by applying a fast rising voltage pulse to electric field plates within the vacuum chamber, and field-ionization electrons emitted were detected by an electron multiplier. To monitor the time-evolution of the Rydberg atoms for quantum beat measurements, the field-ionization signal was measured as a function of a variable delay between the laser excitation and the sampling voltage pulses.

As shown in figure 6, the results of this series of fine-structure measurements on sodium may be summarized by the empirical formula

$$\Delta E(n^2D_{5/2} - n^2D_{3/2})/h = -A/n^{*3} + B/n^{*5}, \quad (18)$$

with $A = 97.8$ (1.1) GHz and $B = 519$ (11) GHz; where $n^* = n - \epsilon$ is the effective quantum number and $\epsilon = 0.014$ is the quantum defect for the sodium d-electron. The continuity of the experimental results, together with Stark-shift quantum beat measurements for $n = 10$ and $n = 11$, show that the fine structure is inverted in all n^2D levels of sodium. The main reason for the inversion of the fine-structure splitting of these levels has long been known to be due to the polarization of the inner core by the outer electron. However, it is only relatively recently that improved theoretical calculations by Luc-Koenig (1976), using a relativistic central-field approximation, have been made precise enough to demonstrate an agreement to

about 10% with the experimental values for the n 2D fine-structure splittings of the $n = 3$ to $n = 16$ levels in sodium.

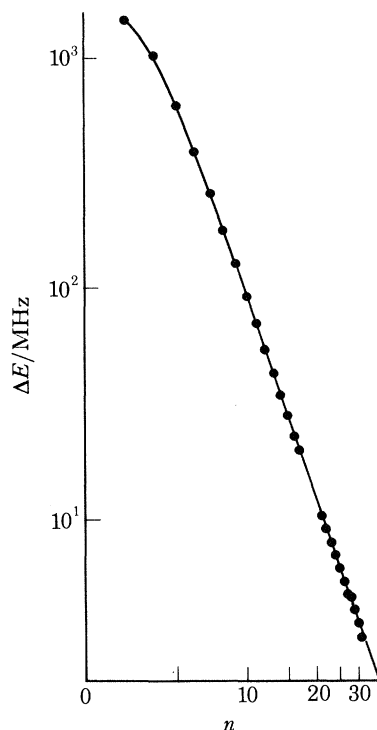


FIGURE 6. The fine-structure splitting of sodium 2D states plotted as a function of principal quantum number (after Leuchs & Walther 1979).

(d) *Transient quantum beat spectroscopy with fast beams*

In quantum beat experiments with pulsed nitrogen laser-pumped dye lasers, the tunable output pulse lasts for *ca.* 4 ns. When this excitation pulse duration is convoluted with a detector rise time of *ca.* 2 ns, which is typical of fast photomultipliers, we find that the methods discussed in §3c are restricted to the measurement of beat frequencies of not more than 100 MHz. To extend the quantum beat technique to higher frequencies, it has until recently been necessary to employ fast ion beams and the methods of beam-foil or beam-laser excitation. In these experiments the resolution time is set by the particle velocity and the observed beam length, and might be *ca.* 50 ps in a typical experiment enabling beats with frequencies not more than 10 GHz to be detected.

The power of these methods has been fully described by Andrä (1978). Here I wish only to call attention to recent quantum beat measurements of the fine-structure intervals of the n 2D levels in lithium, with $n = 4$ to $n = 7$. These measurements have attained an accuracy of $\pm 0.1\%$ and show that a screened hydrogenic variation of $1/n^3$ for the fine-structure splitting in lithium is not sufficient to account for the observed data. These results confirm the need for theoretical fine-structure calculations of even higher accuracy in order to understand the detailed structure of this simplest of three-electron atoms (Wangler *et al.* 1981).

4. TRANSIENT QUANTUM BEATS AND POLARIZATION SPECTROSCOPY

(a) *Monitoring of Hertzian coherences*

In most of the experiments mentioned so far, including both the time-independent level crossing and the transient quantum beat methods, the Hertzian coherence of the ensemble of atoms has been monitored by means of the *spontaneously* emitted fluorescent light. It is only in the last few years that modifications of the pulsed laser quantum beat method have been developed in which the time-evolution of the Hertzian coherences has been monitored by *actively interrogating* the ensemble of atoms. These new techniques include photoionization monitoring (Georges & Lambropoulos 1978; Leuchs *et al.* 1979; Luk *et al.* 1981) and the more efficient field ionization method (Leuchs & Walther 1979) discussed in §3c(ii).

Many physicists seem to have forgotten that, for those atomic levels in which large populations can be created, the optical transmission method for monitoring Hertzian coherences, which was proposed many years ago by Dehmelt (1957) and applied in optical pumping experiments by Bell & Bloom (1957) and Manuel & Cohen-Tannoudji (1963), is extremely sensitive. An obvious modern successor to these early experiments is the method of laser polarization spectroscopy pioneered by Wieman & Hänsch (1976). More recently Lange & Mlynek (1978), in a series of elegant experiments, have modified the laser polarization method so that the time-evolution of Hertzian coherences may be monitored.

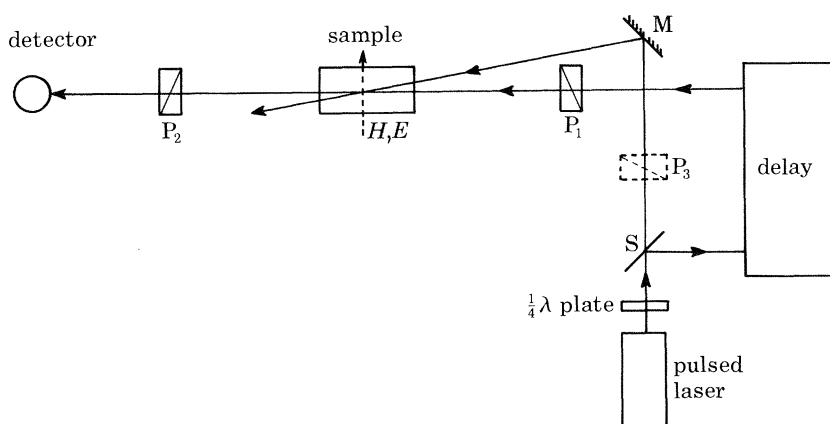


FIGURE 7. Schematic of the experimental arrangement used by Mlynek & Lange (1979) in transmission monitoring of transient quantum beats.

(b) *Transmission monitoring of transient quantum beats with single-pulse lasers*

In the first of these experiments (Lange & Mlynek 1978) a sample of ytterbium atoms was prepared in a coherent superposition of $M_J = \pm 1$ Zeeman substates of the excited 6^3P_1 level by using a pulsed dye laser tuned to the $6^1S_0-6^3P_1$ transition at 557 nm. In the second experiment (Mlynek & Lange 1979) the Hertzian coherence was generated in the ground state of atomic samarium by using a pulsed dye laser tuned to the $4f^6 6s^2 7F_1-4f^6 6s6p 7F_0$ transition at 571 nm. In both investigations a probe pulse, derived from the same laser, was delayed by time $\Delta\tau$ by using an optical delay line, and was sent through the vapour cell almost collinearly with the pump beam, as shown in figure 7. The incident probe pulse is linearly polarized and, in the absence of the pump beam, is prevented from reaching the photomultiplier detector by a crossed polarizer. When the circularly polarized pump and the probe

pulse are sent together through the vapour, the intensity of the light transmitted through the sample shows well resolved quantum beats at twice the Larmor frequency $\omega_L = g_J \mu_B B / \hbar$. The quantum beat signal originating in the lower level, 7F_1 , in samarium is shown in figure 8. In these investigations it was experimentally more convenient to use a fixed delay time and to vary the magnetic induction B applied to the atoms in the cell.

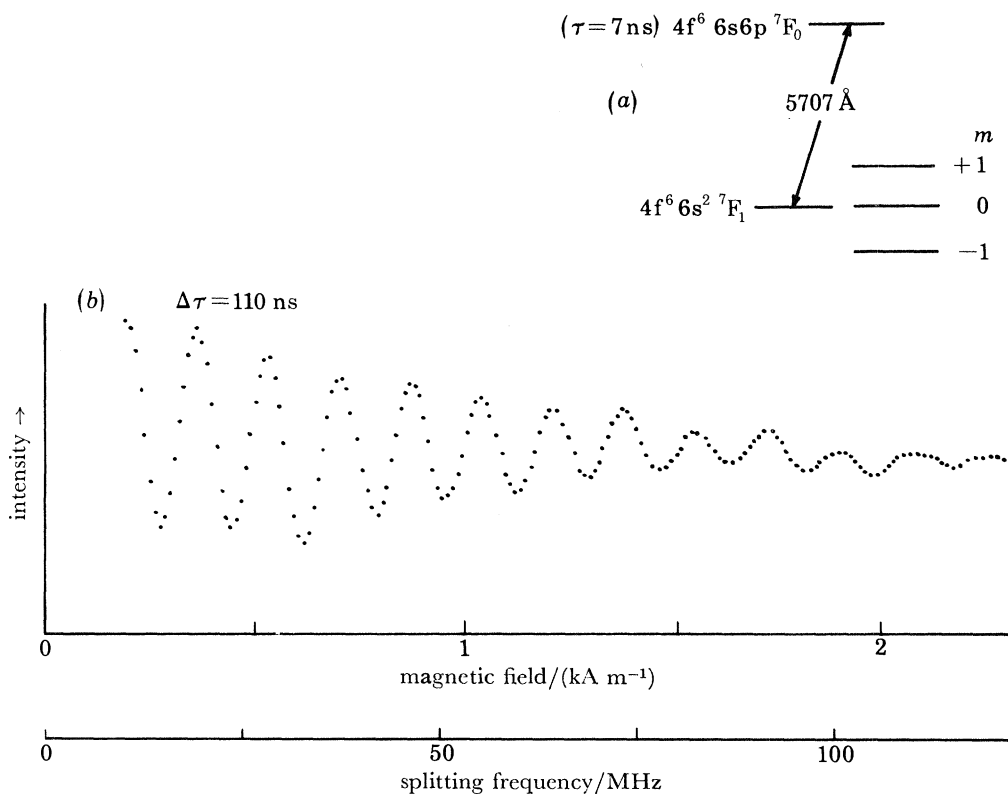


FIGURE 8. (a) Level scheme in samarium. (b) Ground-state Zeeman quantum beats (after Mlynek & Lange 1979).

Physically this technique relies on the complex, time-dependent susceptibility, $\chi(t)$, induced by the incident pump pulse. The pump creates finite Hertzian coherences in the sample, producing anisotropic components in the susceptibility tensor that oscillate at the precessional frequencies of the atomic coherences. The sample now acts as a parametric medium causing the probe beam to acquire frequency sidebands and a modified polarization. When the transmitted probe beam is monitored by a square-law detector, the signal may exhibit beats at the fundamental, and possibly first harmonic, of the precessional frequencies, a phenomenon well known from optical pumping experiments (Happer 1970, 1972).

In the experiments of Lange & Mlynek (1978) the use of a nitrogen laser-pumped dye laser, having a pulse length of *ca.* 5 ns, restricted the detected beat frequency to not more than 100 MHz. However, it would clearly be possible to extend this technique to much higher frequencies by using pulse trains from mode-locked lasers.

(c) *Transmission monitoring with pulse trains from mode-locked lasers*

The feasibility of performing Doppler-free measurements by using pulse trains from lasers was first demonstrated by Teets *et al.* (1977) and Eckstein *et al.* (1978) in two-photon absorption experiments. More recently, periodic excitation with trains of picosecond laser pulses has been used in atomic coherence spectroscopy experiments performed by Mlynek *et al.* (1981a), Harde *et al.* (1981), Harde & Burggraf (1982) and Fukuda *et al.* (1981).

These new high-resolution experiments on ground-state sodium atoms demonstrate an important feature not found in the previous single-pulse transient quantum beat experiments, because the long relaxation times now permit the constructive interference of the contributions from many successive pulses. To show this we assume that the pump pulses arrive at times

$$t_n = nT \quad (n = 0, \pm 1, \pm 2, \dots)$$

where $1/T$ is the pulse repetition frequency. Each pump pulse creates a Hertzian coherence $\rho_{mm'}(0)$, which then evolves in time as

$$\rho_{mm'}^n(t) = \rho_{mm'}(0) \exp \{ -(\gamma + i\omega_{mm'}) (t - nT) \} \quad (t > t_n), \quad (19)$$

where γ is the ground state coherence relaxation rate. This contribution to the ensemble density matrix adds coherently to the contributions created by preceding pulses and the total Hertzian coherence at time t' , $0 \leq t' \leq T$, resulting from the addition of a large number of excitation pulses is

$$\begin{aligned} \rho_{mm'}(t') &= \sum_{n=-\infty}^0 \rho_{mm'}^n(t') \\ &= \rho_{mm'}(0) \left\{ \frac{1 - R \exp(i\omega_{mm'} T)}{(1 - R)^2 + 4R \sin^2(\frac{1}{2}\omega_{mm'} T)} \right\} \exp \{ -(\gamma + i\omega_{mm'}) t' \} \end{aligned} \quad (20)$$

where $R = \exp(-\gamma T)$. Not surprisingly this expression is similar to the Airy function, which describes the transmission resonances of a Fabry-Perot multiple beam interferometer. Equation (20) predicts that resonances in $\rho_{mm'}(t')$ and in the intensity of a probe beam transmitted through the sample will occur whenever $\omega_{mm'} T = 2\pi q$, where $q = 0, 1, 2, \dots$.

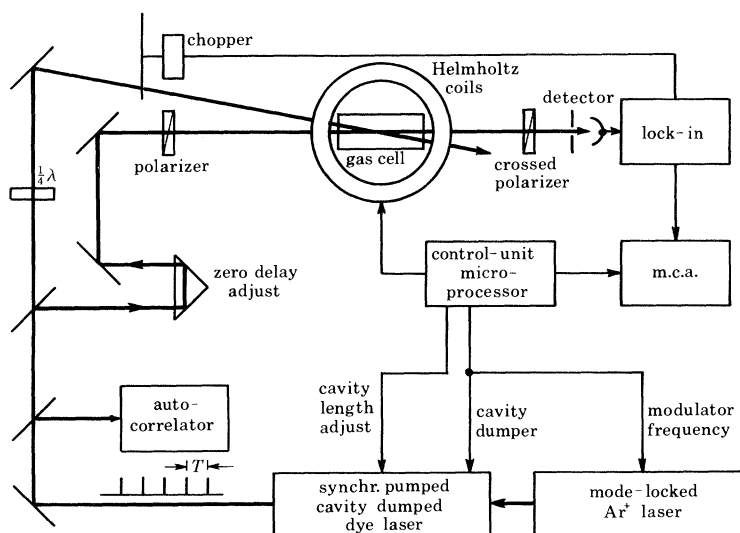


FIGURE 9. Experimental set-up used by Harde & Burggraf (1982) in multiple-pulse quantum beat experiments in the ground state of sodium.

As an example of this technique I show in figure 9 the apparatus used by Harde & Burggraf (1982) in pulse-train quantum beat experiments in the ground state of atomic sodium, $3^2S_{1/2}$. The synchronously pumped mode-locked c.w. dye laser was tuned to the sodium D_1 line and generated picosecond pulses with a repetition frequency of 84 MHz. However, to match a high order of the excitation rate with the precessional frequencies of atomic hyperfine coherences it was advantageous to reduce the pulse rate to 4.2 MHz by using a cavity dumper. The resulting pulse train was split into a strong circularly polarized pump beam and a linearly polarized probe beam. In addition the sodium atoms were subjected to a weak magnetic field parallel to the probe beam polarization to vary the energy separations of the hyperfine Zeeman levels. The intensity transmitted through a crossed polarizer was detected by standard lock-in techniques, and the output of the lock-in was digitized and stored in a multi-channel analyser as a function of the applied magnetic field. The frequency diagram of the $\Delta M_F = \pm 1$ hyperfine energy separations as a function of magnetic field (figure 10a) shows that a sequence of resonances are predicted for harmonics of order $q = 417$ to $q = 424$ for a pulse repetition frequency of 4.21 MHz. Experimental data shown in figure 10b confirm the detection of these resonances.

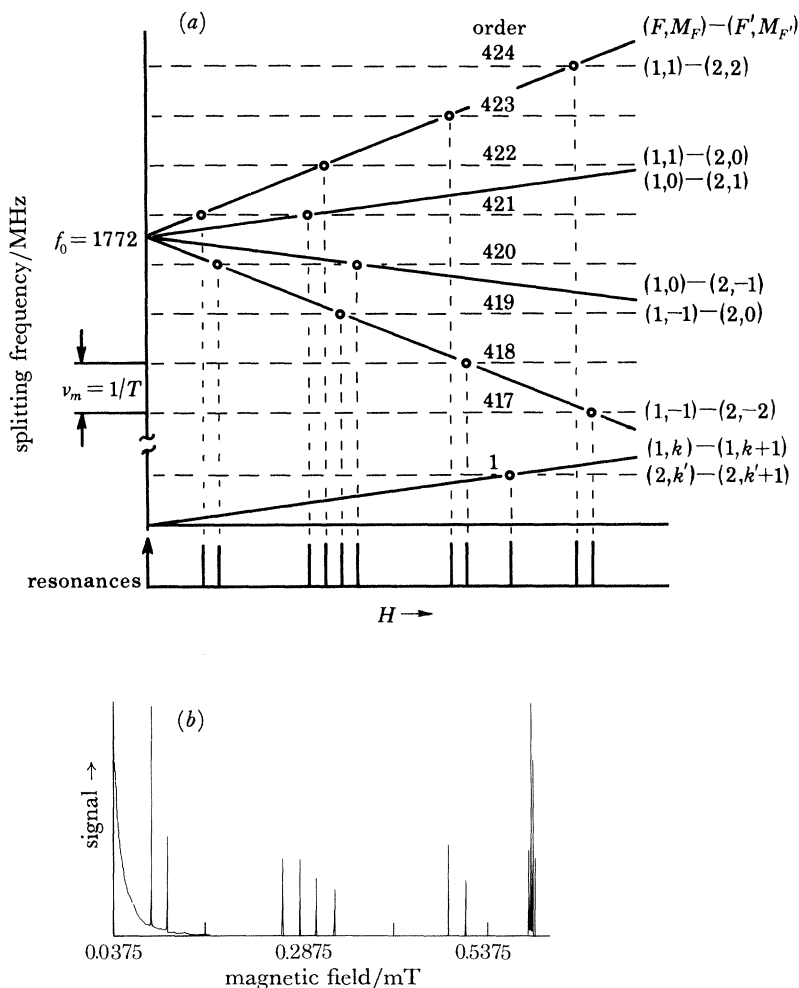


FIGURE 10. (a) Frequency separation of coherently excited levels in the ground state of sodium as a function of applied magnetic field. (b) Experimental polarization anisotropy signal as a function of applied magnetic field; $1/T = \nu_m = 4.21\ 260$ MHz (after Harde & Burggraf 1982).

Further measurements made at even lower repetition rate and on a magnified scan have demonstrated a resonance line-width of less than 1 kHz.

5. CONCLUSION

These exciting new experiments show that the use of pulse trains from mode-locked lasers can remove restrictions imposed by the limited bandwidth of optical detectors on the detection of high-frequency quantum beats; and the upper frequency limit for detectable coherences is now set by the inverse of the laser pulse duration, $1/\Delta t$. The high pulse repetition frequencies used in the multiple-pulse quantum beat technique ensure good signal:noise ratios, and limitations on the accuracy of the transient quantum beat method associated with the calibration and linearity of the time-resolved detection system are now overcome by simple and precise measurements of the excitation pulse repetition frequency. High resolution is ensured by the Doppler-free nature of the Hertzian coherence method, with the line width of the resonances being determined by the relaxation rate of the atomic coherences.

However, the high precision of this new technique is inextricably linked with a complexity of interpretation introduced by overlapping orders, in exactly the same manner as in conventional high-resolution spectroscopy with Fabry–Perot interferometers. In multiple-pulse quantum beat spectroscopy these high-order resonances occur because the train of picosecond pulses contains an extended comb of Fourier harmonics of the pulse repetition frequency. Thus, for the correct interpretation of a complex resonance spectrum, it is necessary to have a good understanding of the expected structure, and this can only be derived from previous measurements at lower resolution.

All these difficulties may be overcome by using light sources whose intensity is modulated at a well defined frequency in the radio or microwave band. Optical excitation then enables sinusoidally driven c.w. quantum beat resonances to be generated, as was demonstrated in early Hertzian Zeeman coherence experiments by Aleksandrov (1963) and Corney & Series (1964*a, b*) with conventional sources and fluorescence monitoring. This work was later extended to resonance experiments on I_2 and Se_2 molecules by Lehmann (1978) and others using modulated laser excitation, but generally this technique has been largely ignored. However, experiments with the use of probe beam monitoring (Snyder *et al.* 1980; Bloch *et al.* 1981) have demonstrated the advantages of employing r.f. modulation and optical heterodyne detection in c.w. laser Doppler-free saturation spectroscopy and these have recently been extended by Mlynek *et al.* (1981*b*) to c.w. quantum beat resonance experiments in atomic sodium. This latest technique in Hertzian coherence spectroscopy retains all the advantages detailed above for the multiple-pulse quantum beat method and has, in addition, the simplicity of a single peak resonance spectrum. Now that methods for r.f. modulating laser beams have been so much improved, the range of possibilities of this c.w. quantum beat method are greatly enhanced and the technique deserves much wider recognition and application.

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Discussion

G. W. SERIES, F.R.S. (*University of Reading, U.K.*). The Hertzian coherence that Dr Corney has described exists between states of the same parity: eigenstates of component of angular momentum in some particular direction (generally chosen to be that of an externally applied magnetic field, if one exists). The coherence arises because the atomic system is prepared by some perturbation having different spatial symmetry: for example, a light beam polarized obliquely to the magnetic field. The coherence is a result of the *broken symmetry*.

I have found the notion of broken symmetry to be very fundamental in thinking about experiments of the sort described by Dr Corney. The symmetry need not always be spatial. For example, if one considers how one might generate experiments based on coherence between states of different parity (S and P levels in hydrogen) one begins to think about CPT conservation, then about the need for an electric field, then about the need for breaking the T symmetry. This leads to the notion of pulsed or modulated excitation of atoms in an E -field as a condition for coherence. (Of course, although Dr Corney has described pulse experiments in the context of breaking *spatial* symmetry, the pulsing was not of the essence: steady-state versions of the phenomena he described can be envisaged. For states of opposite parity in an electric field, pulsing or modulation is of the essence (G. W. Series (1964) *Phys. Rev.* **136**, A684–688, section 5).)