Theory of modulation of light in a double resonance experiment

By J. N. Dodd†

Department of Physics, University of Otago, Dunedin, New Zealand,

and G. W. Series

Clarendon Laboratory, University of Oxford

A theory is formulated to describe the modulation which has been observed in fluorescent light from atoms subjected simultaneously to optical and radio-frequency radiation. The optical field stimulates one or more of a set of excited states of the atom, between which the radio-frequency field establishes coherence. This coherence is manifest in the fluorescent radiation. Interference between radiations of different frequency leads to modulation. General expressions are given for the intensity of the fluorescent light as a function of time. The Zeeman structure of the transition $(6^3P_1 - 6^1S_0)$, $\lambda 2537$ Å, in mercury is studied in detail. Modulation at frequencies, 1, 2, 3 and 4 times that of the radio-frequency field, ω_0, is predicted, and resonant effects at static magnetic fields, 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, 2 and 3 times H_0, the field for which ω_0 is the Larmor frequency. Resonances at fields other than H_0 are due to excitation with light of mixed polarization. Most of the predicted effects have been found experimentally.

A 'frequency diagram' is introduced and discussed, to represent the combined effects of static and radio-frequency magnetic fields. To each excited state belong a set of r frequencies, where r is the number of states linked by the radio-frequency perturbation. The 9 levels are drawn, as functions of H, for the states $m_J = 0$, ± 1, of $^3P_1$. The resonances at fields other than H_0 may be associated with intersections of frequency levels belonging to different m_J.

1. Introduction

It has been shown experimentally that the fluorescent light in a double resonance experiment is strongly modulated (Dodd, Fox, Series & Taylor 1959). A theory of the phenomenon is presented in this paper.

In a double resonance experiment, free atoms are subjected simultaneously to optical and radio-frequency radiations, both of which are near to resonant frequencies of the atoms. The first experiment of this type (Brossel & Bitter 1952) was performed with mercury vapour situated in a uniform magnetic field. Optical radiation at 2537 Å excited the atoms from the ground state, $^1S_0$, to the state $m = 0$ of the level $^3P_1$, from which transitions to $m = \pm 1$ were induced by a radio-frequency field at the Larmor frequency. The transitions were detected by the changes which they brought about in the polarization and spatial distribution of the fluorescent light.

A complete description of the response of the atoms to the electromagnetic fields cannot, however, be given simply in terms of populations of states, but must take account of the fact that the occupation probabilities are not independent. The phases of the probability amplitudes are related to the phase of the radio-frequency field,

† On leave at the Clarendon Laboratory, Oxford, 1959.

and hence to one another. In the fluorescent light, the coherence between the excited states is manifest as interference between optical radiations of different frequencies. It is this interference, giving rise to modulation, which was detected in the experiments of Dodd *et al.*

In this paper, and in that of Barrat which follows, the problem is formulated in terms of probability amplitudes. Related phenomena have been interpreted in other ways. Under similar conditions of irradiation of an atomic vapour with optical and radio-frequency fields, Bell & Bloom (1957) detected modulation in the absorbed light. Following Dehmelt's suggestion (1957) they used a phenomenological model, based on the Bloch equations, to interpret their experiments. We believe that the two sets of experiments are the emission and absorption counterparts of each other, and that both can be legitimately described either by the quantum-mechanical or by the phenomenological model

In the following sections we calculate the intensity of light scattered by a single atom, and assume that there is no coherence between light scattered by different atoms. This is justifiable only to the extent that we are concerned with laterally scattered radiation whose wavelength is very much smaller than the mean distance between neighbouring atoms. We assume also that there is no multiple scattering. The assumption that different atoms radiate incoherently allows us to ignore the dependence of phase on the position of the scattering centre. The size of the sample is small compared with the wavelength at radio-frequencies.

The calculations in this paper have been carried through with particular reference to the transition $(6^3P_1 - 6^1S_0)$, $\lambda 2537 \,\text{Å}$ in mercury, where the radio-frequency mixing is taking place between the Zeeman states of the upper level. This is a particularly simple case in that the three excited states are equally spaced in energy and are damped at the same rate, and in that there is only one ground state. The principles of the calculation could be applied to other situations: for example, the radio-frequency transitions could be between multiplet or hyperfine states. When radio-frequency mixing in the ground states is to be studied, some assumption concerning phase memory would have to be made, equivalent to that of introducing radiative damping into the excited state.

2. Formulation of the problem

Consider an atom in a uniform magnetic field **H**. Of the possible eigenstates we shall be concerned only with a non-degenerate ground state $|g\rangle$ and a set of excited states $|m\rangle$ which belong to a particular level of angular momentum **J**. It is supposed that the states $|m\rangle$, and no others, are accessible from $|g\rangle$ by optical excitation, owing to the limited spectral range of the light. The $|m\rangle$ are connected with one another by the radio-frequency perturbation.

In order to avoid unnecessary complication, the particular value $J = 0$ is chosen for $|g\rangle$. Since this restriction may readily be lifted, we prefer not to impose on the excited states the restrictions on J which electric dipole transitions from $|g\rangle$ would require.

(i) *The states and the Hamiltonians*

The state of the atom, $|t\rangle$, at any time t satisfies the equation

$$i\hbar \, d|t\rangle/dt = \mathscr{H}|t\rangle, \tag{1}$$

where the Hamiltonian $\mathscr{H}$ may be written, to describe the type of experiment we are considering,

$$\mathscr{H} = \mathscr{H}_0 + \gamma \mathbf{J}.\mathbf{H} + \mathscr{H}_D + \mathscr{H}_{\text{r.f.}} + \mathscr{H}_{\text{opt.}} \tag{2}$$

The first two terms on the right describe the interactions within the atom and the effect of the field $\mathbf{H}$; γ is the gyromagnetic ratio.

The third term describes the radiative damping of the excited states. We assume that the matrix of $\mathscr{H}_D$ is diagonal, with elements $-\frac{1}{2}i\hbar\Gamma$ for the states $|m\rangle$, and zero for $|g\rangle$.

The fourth and fifth terms describe the radio-frequency and optical perturbations, respectively. These are formulated semi-classically, and discussed in detail below.

The state of the atom may be expressed as a superposition of states independent of time by the expansion

$$|t\rangle = \sum_m a_m(t)\,|m\rangle + a_g(t)\,|g\rangle. \tag{3}$$

Explicit forms for the a_m and a_g are found by solving the equation of motion, given that the atom is initially in the state $|g\rangle$.

(ii) *Method of solution*

Since the optical excitation is weak ($a_g \approx 1$ at all times), we can treat $\mathscr{H}_{\text{opt.}}$ as a small perturbation and write $\mathscr{H} = \mathscr{H}^* + \mathscr{H}_{\text{opt.}}$, where

$$\mathscr{H}^* = \mathscr{H}_0 + \gamma \mathbf{J}.\mathbf{H} + \mathscr{H}_D + \mathscr{H}_{\text{r.f.}}.$$

Let $|\,\rangle$ symbolize a state of the system at time t which would evolve from the state $|t_0\rangle$ under the influence of $\mathscr{H}^*$ only. The equation of motion of this state is

$$i\hbar \, d|\,\rangle/dt = \mathscr{H}^*|\,\rangle, \tag{4}$$

with the condition $|\,\rangle = |t_0\rangle$ when $t = t_0$. The transformation from $|t_0\rangle$ to $|\,\rangle$ may conveniently be expressed by defining an operator $U(t, t_0)$ as follows:

$$U(t, t_0)\,|t_0\rangle = |\,\rangle. \tag{5}$$

It is then readily verified that $|t\rangle$, the solution of (1) may be written

$$|t\rangle = U(t, 0)|0\rangle + \frac{1}{i\hbar}\int_0^t dt_0 \, U(t, t_0)\, \mathscr{H}_{\text{opt.}}(t_0)\, U(t_0, 0)\,|0\rangle \tag{6}$$

$$+ \text{ terms of second order in } \mathscr{H}_{\text{opt.}}.$$

With the use of explicit expressions for $\mathscr{H}_{\text{opt.}}$ and U which are to be obtained in section (3), equation (6) may be expanded in the form of equation (3), thereby obtaining the coefficients $a_m(t) \equiv \langle m|t\rangle$. The precise value of $a_g(t)$ is not of particular interest, provided it does not depart greatly from unity.

23-2

It remains to calculate the intensity of the fluorescent light as a function of time. This is proportional to the modulus squared of the matrix element of the electric dipole operator $\mathbf{P}$ between the states $|t\rangle$ and $|g\rangle$. The result, and its justification by a Correspondence argument, is given in §4.

3. Solution of the equation of motion

(i) The operator $\mathscr{H}_{\mathrm{opt}}$.

Let the electric field of the incident light at time t be $\mathbf{E}_i(t) = E_i(t)\,\mathbf{e}_i^0$, where $\mathbf{e}_i^0$ is a unit vector representing the direction of polarization. We shall see in due course that $E_i(t)$ need not be completely specified: the significant quantity is the real correlation function $\langle E_i(t)\,E_i(t+\tau)\rangle$. This will ultimately be chosen to represent a steady beam of light of spectral width greater than any of the frequency differences with which we are concerned, in the neighbourhood of the excitation frequencies of the states $|m\rangle$.
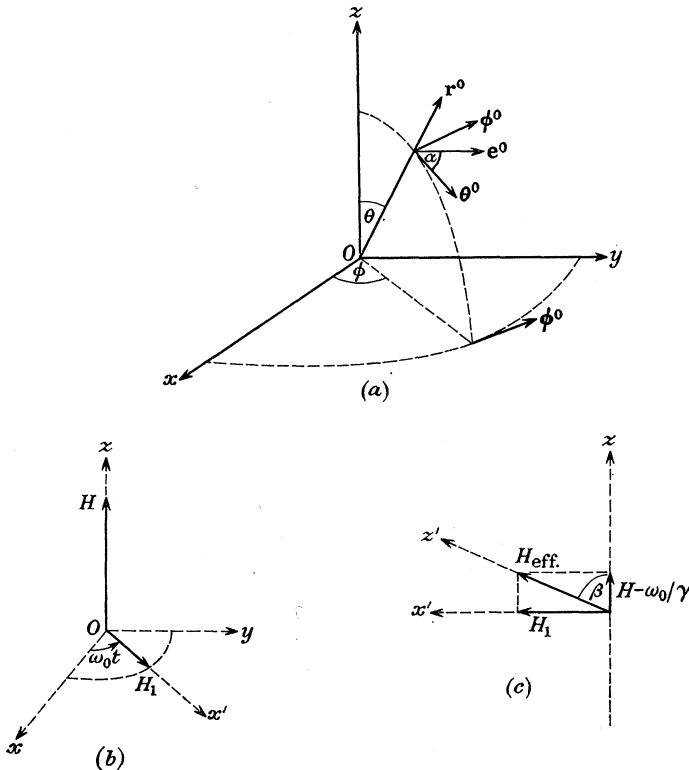
FIGURE 1. The notation.

The operator $\mathscr{H}_{\mathrm{opt}}$. we consider only in the first approximation, in which it is the scalar product $\mathbf{E}_i . \mathbf{P}$, where $\mathbf{P}$ is the electric dipole operator. We shall write

$$\mathscr{H}_{\mathrm{opt}}. = E_i(t)\,\mathbf{e}_i^0 . \mathbf{P} \equiv E_i(t)\,F. \tag{7}$$

The only matrix elements of F which do not vanish are those between the excited states $|m\rangle$ and the ground state $|g\rangle$; we write them as $F_m \equiv \langle m|\,F\,|g\rangle$.

For later reference we expand $\mathbf{e}^0$. Let the direction of the light be specified by θ, ϕ (figure 1(a)), and let the electric vector make an angle α with the unit vector associated with θ. Then

$$\mathbf{e}^0 = \mathbf{i}(\cos\theta\cos\phi\cos\alpha - \sin\phi\sin\alpha)$$
$$+ \mathbf{j}(\cos\theta\sin\phi\cos\alpha + \cos\phi\sin\alpha) \tag{8}$$
$$+ \mathbf{k}(-\sin\theta\cos\alpha).$$

(ii) *The operator U*

Through equations (4) and (5), U is related to

$$\mathscr{H}^* = \mathscr{H}_0 + \gamma\mathbf{J}.\mathbf{H} + \mathscr{H}_D + \mathscr{H}_{\mathrm{r.f.}}.$$

We are interested in the effect of a radio-frequency field of amplitude H_1 rotating with angular velocity ω_0 in a plane perpendicular to $\mathbf{H}$, the z-direction (figure 1(b)). The perturbation operator is

$$\mathscr{H}_{\mathrm{r.f.}} = \gamma\mathbf{J}.\{(H_1\cos\omega_0 t)\,\mathbf{i} + (H_1\sin\omega_0 t)\mathbf{j}\}. \tag{9}$$

With this form for $\mathscr{H}_{\mathrm{r.f.}}$, the Hamiltonian $\mathscr{H}^*$ may be written (Salwen 1955, for example)

$$\mathscr{H}^* = \exp\{(-iJ_z\omega_0 t/\hbar)\}\,\mathscr{H}_1\{\exp(iJ_z\omega_0 t/\hbar)\}, \tag{10}$$

where

$$\mathscr{H}_1 = \mathscr{H}_0 + \mathscr{H}_D + \gamma H J_z + \gamma H_1 J_x. \tag{11}$$

It is convenient to make a unitary transformation T to a co-ordinate system $Ox'y'z$ rotating about Oz with angular velocity ω_0. This transforms $\mathscr{H}^*$ to $\mathscr{H}_1$, and $|\rangle$ into $|'\rangle = \exp(iJ_z\omega_0 t/\hbar)|\rangle$. The equation of motion (4) now becomes (Rabi, Ramsey & Schwinger 1954)

$$i\hbar\,d|'\rangle/dt = (\mathscr{H}_1 - \omega_0 J_z)|'\rangle = \mathscr{H}'|'\rangle, \tag{12}$$

where

$$\mathscr{H}' = \mathscr{H}_0 + \mathscr{H}_D + \delta J_z + bJ_x, \tag{13}$$

in which

$$\delta = \omega - \omega_0, \quad \omega = \gamma H \quad \text{and} \quad b = \gamma H_1.$$

The Hamiltonian $\mathscr{H}'$ is now independent of time, and the equation of motion (12) may readily be solved giving

$$|'\rangle = \exp\{(\mathscr{H}'/i\hbar)(t - t_0)|'t_0\rangle\}, \tag{14}$$

where the state $|'\rangle$ at $t = t_0$ is written $|'t_0\rangle$.

By applying the inverse transformation, T^{-1}, to $|'\rangle$ and $|'t_0\rangle$, we find the relation between $|\rangle$ and $|t_0\rangle$, which, by comparison with equation (5), yields

$$U(t, t_0) = \exp(-iJ_z\omega_0 t/\hbar)\exp\{(\mathscr{H}'/i\hbar)(t - t_0)\}\exp(iJ_z\omega_0 t_0/\hbar). \tag{15}$$

In the evaluation of the intensity of fluorescent radiation, we shall need the matrix elements $U_{mn} \equiv \langle m|U|n\rangle$ taken between any two of the excited states $|m\rangle$ and $|n\rangle$ (the letter n is used for possible values of m to avoid difficulties in notation created by the use of subscripts and primes). The U_{mn} are obtained from the eigenstates and eigenvalues of J_z and $\mathscr{H}'$.

The eigenstates of J_z are $|g\rangle$ and $|m\rangle$, with eigenvalues 0 and $m\hbar$, respectively.

The eigenstates of $\mathscr{H}'$ are most easily expressed in terms of a co-ordinate system produced by a rotation of Oz about Oy' by an angle $\beta = \tan^{-1}(b/\delta)$ (figure 1 (c)). $\mathscr{H}'$ may then be written $\mathscr{H}_0 + \mathscr{H}_D + p J_{z'}$ where $p = (\delta^2 + b^2)^{\frac{1}{2}}$. As the field H increases from zero, through the resonant field $H_0 = \omega_0/\gamma$, to infinity, the angle β passes from the value π, through $\frac{1}{2}\pi$ to zero. The eigenvalues of $\mathscr{H}'$ are

$$0 \quad \text{and} \quad \hbar\lambda_\mu = \hbar(k_0 - \tfrac{1}{2}\mathrm{i}\Gamma + \mu p),$$

corresponding respectively to the eigenstates $|\gamma\rangle$ and $|\mu\rangle$ of the atom in $H_{\text{eff.}}$, the effective field in the rotating co-ordinate system. The states $|m\rangle$ and $|\mu\rangle$, $|g\rangle$ and $|\gamma\rangle$ are related by the linear transformations

$$|\mu\rangle = \sum_m \langle m|\mu\rangle |m\rangle = \sum_m \mathscr{D}^J(0,\beta,0)_{m\mu}|m\rangle; \quad |\gamma\rangle = |g\rangle, \tag{16}$$

where the $\mathscr{D}^J(0,\beta,0)_{m\mu}$ are elements of the rotation matrix (Rose 1957, for example).

Using these results we obtain

$$\begin{aligned}
U_{mn}(t,t_0) &= \langle m|\exp(-\mathrm{i}J_z\omega_0 t/\hbar)\exp(\mathscr{H}'/\mathrm{i}\hbar)(t-t_0)\exp(\mathrm{i}J_z\omega_0 t_0/\hbar)|n\rangle \\
&= \exp(-\mathrm{i}m\omega_0 t)\exp(\mathrm{i}n\omega_0 t_0)\sum_\mu \langle m|\mu\rangle\langle\mu|\exp(\mathscr{H}'/\mathrm{i}\hbar)(t-t_0)|n\rangle \\
&= \exp(-\mathrm{i}m\omega_0 t)\exp(\mathrm{i}n\omega_0 t_0)\sum_{\mu,\nu}\langle m|\mu\rangle\langle\mu|\exp(\mathscr{H}'/\mathrm{i}\hbar)(t-t_0)|\nu\rangle\langle\nu|n\rangle \\
&= \exp(-\mathrm{i}m\omega_0 t)\exp(\mathrm{i}n\omega_0 t_0)\sum_\mu \langle m|\mu\rangle\langle\mu|n\rangle\exp\{-\mathrm{i}\lambda_\mu(t-t_0)\}, \tag{17}
\end{aligned}$$

since the $|\mu\rangle$ are eigenstates of $\mathscr{H}'$.

(iii) Expansion of the state $|t\rangle$

We are now in a position to find the coefficients $a_m(t)$ of equation (3). From equation (6) we find, by forming the bracket product with $|m\rangle$,

$$a_m(t) \equiv \langle m|t\rangle = \langle m|U(t,0)|0\rangle + (1/\mathrm{i}\hbar)\int_0^t \mathrm{d}t_0 \langle m|U(t,t_0)\mathscr{H}_{\text{opt.}}(t_0)U(t_0,0)|0\rangle, \tag{18}$$

in which $|0\rangle$, the state at $t=0$, is simply $|g\rangle$. Since $|g\rangle$ is an eigenstate of J_z with eigenvalue 0, and since $|\gamma\rangle = |g\rangle$ is an eigenstate of $\mathscr{H}'$ with eigenvalue 0, $|g\rangle$ is also an eigenstate of U with eigenvalue 1 for all t. Hence the first term on the right of equation (18) is $\langle m|g\rangle = 0$, and the second term reduces to

$$(1/\mathrm{i}\hbar)\int_0^t \mathrm{d}t_0 \langle m|U(t,t_0)\mathscr{H}_{\text{opt.}}(t_0)|g\rangle.$$

With the use of equation (7) this becomes

$$(1/\mathrm{i}\hbar)\int_0^t \mathrm{d}t_0 E_i(t_0)\sum_n F_n\langle m|U(t,t_0)|n\rangle. \tag{19}$$

Finally, from (17), (19) and (3) we have

$$\begin{aligned}
|t\rangle = a_g|g\rangle + (1/\mathrm{i}\hbar)\int_0^t &\mathrm{d}t_0 E_i(t_0)\sum_{m\mu n}\langle m|\mu\rangle\langle\mu|n\rangle F_n \\
&\times \exp(-\mathrm{i}m\omega_0 t)\exp\{-\mathrm{i}\lambda_\mu(t-t_0)\}\exp(\mathrm{i}n\omega_0 t_0)|m\rangle. \tag{20}
\end{aligned}$$

The physical meaning of the second term on the right is simply the following: the coefficient $(1/i\hbar) E_i(t_0) F_n \, \mathrm{d}t_0$ represents the probability amplitude of the state $|n\rangle$ when the optical perturbation acts on an atom in state $|g\rangle$ (which is approximately the state $|t_0\rangle$) for a time $\mathrm{d}t_0$ at t_0; the coefficient

$$\sum_{\mu} \langle m|\mu\rangle \langle \mu|n\rangle \exp\left(-im\omega_0 t\right) \exp\left\{-i\lambda_\mu(t-t_0)\right\} \exp\left(in\omega_0 t_0\right)$$

represents the probability amplitude of the state $|m\rangle$ at time t when the radio-frequency and damping perturbations have acted for a time $(t-t_0)$ on an atom which, at time t_0, was in the state $|n\rangle$; (this coefficient, in a different form, and without the radiative damping, was derived by Majorana (1932) (see also Ramsey 1956, appendix E); the combined coefficients, summed over the m, μ and n, and integrated over t_0, represent the net effect of optical, radio-frequency and damping perturbations in an approximation in which the excitation rate is weak compared with the rate of spontaneous decay, that is to say, the probability of finding the atom in the ground state is always very much greater than the probability of finding it excited ($a_g \approx 1$).

4. THE FLUORESCENT RADIATION

(i) *Calculation of the intensity I*

The energy flux per unit area of radiation in an electromagnetic field specified by the complex vectors $\mathbf{E}$, $\mathbf{H}$, is given by

$$\mathbf{S}_{\mathrm{av.}} = c(\mathbf{E} \wedge \mathbf{H}^* + \mathbf{E}^* \wedge \mathbf{H})/16\pi.$$

Using $\mathbf{H} = \mathbf{r}^0 \wedge \mathbf{E}$ for electromagnetic waves propagated in the direction of the unit vector $\mathbf{r}^0$, one obtains

$$\mathbf{S}_{\mathrm{av.}} = I\mathbf{r}^0 = c(\mathbf{E}^* . \mathbf{E}/8\pi)\,\mathbf{r}^0. \tag{21}$$

The radiation field $\mathbf{E}(r, \theta, \phi, t)$, to first approximation, is related to the matrix element $\langle g| P |t\rangle$ by

$$\mathbf{E} = (2k^2/rc^2) \langle g|\, \mathbf{P} - (\mathbf{r}^0 . \mathbf{P})\, \mathbf{r}^0 \,|t\rangle. \tag{22}$$

Its component in the direction $\mathbf{e}^0$, which lies in the plane normal to $\mathbf{r}^0$ (see figure 1(a)) is

$$\mathbf{e}^0 . \mathbf{E} = (2k^2/rc^2) \langle g|\, \mathbf{e}^0 . \mathbf{P} \,|t\rangle. \tag{23}$$

Equation (22) may be derived by a Correspondence argument (see, for example, Condon & Shortley 1951, pp. 89, 90) when the states concerned are pure states of a time-independent Hamiltonian. Its application when $|t\rangle$ is expressed as a linear superposition of such states may be justified from the superposition theorem for electric fields.

The expression for I thus depends on the form of the matrix elements $\langle g|\, \mathbf{e}^0 . \mathbf{P} \,|t\rangle$, which, are, by equation (20)

$$\langle g|\mathbf{e}^0 . \mathbf{P}|t\rangle = (1/i\hbar) \int_0^t \mathrm{d}t_0\, E_i(t_0) \sum_{m\mu n} G_m^* \langle m|\mu\rangle \langle \mu|n\rangle F_n$$
$$\times \exp\left(-im\omega_0 t\right) \exp\left\{-i\lambda_\mu(t-t_0)\right\} \exp\left(in\omega_0 t_0\right), \quad (24)$$

in which we have introduced $G_m^* = \langle g|\mathbf{e}^0 . \mathbf{P}|m\rangle$. By this definition F_m and G_m are defined identically except for the direction of the polarization vector.

Combining equations (21), (23) and (24) we arrive at the following expression for the intensity of light at time t, plane polarized in the direction $\mathbf{e}^0$, due to the scattering from one atom:

$$I = \frac{k_0^4}{2\pi c^3 \hbar^2 r^2} \int_0^t dt_0 E_i(t_0) \sum_{m\mu n} G_m^* \langle m|\mu\rangle \langle \mu|n\rangle F_n \exp(-im\omega_0 t)$$
$$\times \exp\{-i\lambda_\mu(t-t_0)\} \exp(in\omega_0 t_0)$$
$$\times \int_0^t dt_0' E_i(t_0') \sum_{m'\mu'n'} F_{n'}^* \langle n'|\mu'\rangle \langle \mu'|m'\rangle G_{m'} \exp(im'\omega_0 t) \exp\{i\lambda_{\mu'}^*(t-t_0')\}$$
$$\times \exp(-in'\omega_0 t_0'), \qquad (25)$$

in which k_0 is an average optical frequency. For laterally scattered radiation from N atoms the expression is to be multiplied by N and $(1/r^2)$ replaced by a mean value, $(1/r_0^2)$.

The dependence on t, t_0 and t_0' of the terms in equation (25) is of the form

$$\exp\{-i(m-m'-n+n')\omega_0 t\} \int_0^t dt_0 \exp\{-(\Gamma+ix)(t-t_0)\} \int_0^t dt_0' E_i(t_0) E_i(t_0')$$
$$\times \exp\{-(\tfrac{1}{2}\Gamma-ik')(t_0-t_0')\} \quad (26)$$

in which $\qquad k' = k_0 + \mu'p + n'\omega_0 \quad$ and $\quad x = (\mu-\mu')p + (n-n')\omega_0.$ $\qquad (27)$

In order to evaluate the double integral it is not necessary to specify the field $E_i(t_0)$ itself, nor even the product $\Phi(t_0,\tau) = E_i(t_0) E_i(t_0+\tau)$, where $\tau = (t_0-t_0')$. It is sufficient to know the average value $\langle\Phi(t_0,\tau)\rangle$, taken with fixed τ over a time, centred on t_0, which covers many periods of the optical frequency k'. To see this, notice that the only term in (26), apart from Φ, which oscillates rapidly, is $\exp - (\tfrac{1}{2}\Gamma-ik')\tau$. Now fix τ, and integrate over a range of t_0 large compared with $1/k'$ but small compared with $(\Gamma^2+x^2)^{\frac{1}{2}}$. The only quantity which changes appreciably during this time is Φ. The value of (26) is therefore unchanged if we substitute for Φ the mean value

$$\langle\Phi(t_0,\tau)\rangle = \frac{1}{2T_0} \int_{t_0-T_0}^{t_0+T_0} \Phi(t,\tau)\,dt.$$

The advantage of introducing $\langle\Phi\rangle$ is that it is closely related to a quantity which can actually be measured, the power spectrum of the incident light.

Several cases now can be distinguished:

(i) The intensity of the exciting light is independent of time, as in the ordinary double resonance experiment. In this case $\langle\Phi\rangle$ is the auto-correlation function for stationary fields. It is a function of τ only, not of t_0, and is related to the power spectrum $\rho(k)$:

$$\langle E_i(t_0) E_i(t_0')\rangle = \langle\Phi(\tau)\rangle = \frac{8\pi}{c} \int_{-\infty}^{+\infty} dk\,\rho(k)\exp(-ik\tau), \qquad (28)$$

(see, for example, Born & Wolf 1959, p. 501; the factor $\exp(-2\pi i\nu t)$ in their equation (27) should read $\exp - 2\pi i\nu\tau$).

(ii) The exciting light is modulated or pulsed. In this case $\langle\Phi\rangle$ is a function of t_0 as well as of τ. We shall not pursue the analysis of this case, but refer to it again at the end of §6.

Returning to case (i) and inserting (28) into (26), we find that the integral over t_0' may be expressed

$$\frac{8\pi}{c}\int_{t_0-t}^{t_0} d\tau \exp\left(-\tfrac{1}{2}\Gamma\tau\right)\int_{-\infty}^{+\infty} dk\,\rho(k)\exp\left\{-\mathrm{i}(k-k')\tau\right\}. \tag{29}$$

Again, we distinguish cases for which $\rho(k)$ has different forms:

(*a*) Monochromatic light of angular frequency k'. In this case the form of $\rho(k)$ is $R\delta(k-k')$, the double integral (29) becomes $(16\pi R/c\Gamma)\exp\tfrac{1}{2}\Gamma(t-t_0)$ for $t_0 \gg 1/\Gamma$, and (26) reduces to

$$\frac{16\pi R}{c\Gamma}\frac{1}{(\tfrac{1}{2}\Gamma+\mathrm{i}x)}\exp\left\{-\mathrm{i}(m-m'-n+n')\,\omega_0 t\right\}. \tag{30}$$

(*b*) White light. In this case $\rho(k)=\rho_0$, independent of k, the integral over k in (29) becomes $\rho_0\delta(\tau)$, the value of (29), $8\pi\rho_0/c$, and (26) reduces to

$$\frac{8\pi\rho_0}{c}\frac{1}{(\Gamma+\mathrm{i}x)}\exp\left\{-\mathrm{i}(m-m'-n+n')\,\omega_0 t\right\}. \tag{31}$$

(*c*) Quasi-monochromatic light of mean angular frequency k' and spectral width $\Delta \gg \Gamma$, such as was used in the experiments. In this case $\rho(k)$ might take the form, for example, $\rho_0\exp\left\{-(k-k')^2/\Delta^2\right\}$. More important than the exact form of $\rho(k)$, provided it is a slowly varying function, is the time $\tau_\Delta \approx 1/\Delta$ over which coherence persists in the optical field, for if τ_Δ is much less than the lifetime of the atoms, then we find the same result as for white light, as may readily be shown:

Choose a time τ_0 such that $1/\Delta \ll \tau_0 \ll 1/\Gamma$. Now the integral over k in (29) behaves like $\rho_0\delta(k-k')$ except in the region $|\tau| < \tau_0$. Inside this region we may, to a good approximation, replace $\exp-\tfrac{1}{2}\Gamma\tau$ by unity. The expression (29) thus has the value, in this case,

$$\frac{8\pi}{c}\int_{t_0-t}^{t_0} d\tau \int_{-\infty}^{+\infty} dk\,\rho(k)\exp\left\{-\mathrm{i}(k-k')\tau\right\} = \frac{8\pi}{c}\int_{-\infty}^{+\infty} dk\,\rho(k)\int_{t_0-t}^{t_0} d\tau \exp\left\{-\mathrm{i}(k-k')\tau\right\}$$

$$= \frac{8\pi}{c}\int_{-\infty}^{+\infty} dk\,\rho(k)\,\delta(k-k') = \frac{8\pi}{c}\rho(k')$$

from which the expression (26) again reduces to (31), the result obtained for white light.

If the spectral range of the light not only greatly exceeds Γ, but also spans all possible values of k' in equation (27), equation (25) becomes, for N atoms,

$$I = \frac{4Nk_0^4}{\Gamma c^4\hbar^2 r_0^2}\rho(k_0)\sum_{\substack{m\mu n\\ m'\mu'n'}} \mathscr{F}_{nn'}\langle m|\mu\rangle\langle\mu|n\rangle\langle n'|\mu'\rangle\langle\mu'|m'\rangle\mathscr{G}_{mm'}\frac{\Gamma}{\Gamma+\mathrm{i}x}$$
$$\times \exp\left\{-\mathrm{i}(m-m'-n+n')\,\omega_0 t\right\}, \tag{32}$$

where m,μ,n,m',μ',n' take the values $-J,-J+1,\ldots+J$. We have introduced the notation $\mathscr{F}_{nn'} = F_n F_{n'}^*$, $\mathscr{G}_{mm'} = G_m^* G_{m'}$, where F and G, it will be recalled, refer to excitation by, and the observation of, plane polarized light

$$F_n = \langle n|\mathbf{e}_i^0.\mathbf{P}|g\rangle, \quad G_m = \langle m|\mathbf{e}^0.\mathbf{P}|g\rangle.$$

For convenience, we here repeat the definitions of the other symbols

$$\langle m|\mu\rangle = \mathcal{D}^J(0,\beta,0)_{m\mu}; \quad x = (\mu-\mu')\,p + (n-n')\,\omega_0; \quad p = (\delta^2+b^2)^{\frac{1}{2}};$$

$$b = \gamma H_1; \quad \delta = \omega-\omega_0; \quad \omega = \gamma H; \quad \beta = \tan^{-1}(b/\delta);$$

and $\rho(k_0)$ is the energy flux of the incident light per unit area, per unit spectral range.

The elements $\mathcal{F}_{nn'}$, and $\mathcal{G}_{mm'}$ form what may be termed the excitation and emission matrices, respectively. They may be generalized to unpolarized light, and to polarized light other than plane. Thus, for unpolarized light, the matrix element $\mathcal{F}^u_{nn'}$ may be formed by adding to $(F_n F^*_n)$ the element formed by using the polarization vector perpendicular to $\mathbf{e}^0_i$. Introducing the unit vectors $\mathbf{r}^0$, $\boldsymbol{\theta}^0$ and $\boldsymbol{\phi}^0$ (figure 1 (a)), we define

$$\mathbf{F}_n = \langle n|\,\mathbf{P} - (\mathbf{r}^0.\mathbf{P})\,\mathbf{r}^0|g\rangle = \langle n|(\boldsymbol{\theta}^0.\mathbf{P})\,\boldsymbol{\theta}^0 + (\boldsymbol{\phi}^0.\mathbf{P})\boldsymbol{\phi}^0|g\rangle. \tag{33a}$$

Then we have for unpolarized light,

$$\mathcal{F}^u_{nn'} = \mathbf{F}_n.\mathbf{F}^*_n, \tag{33b}$$

and for circularly polarized light

$$\mathcal{F}^c_{nn'} = F^c_n F^{*c}_n, \tag{33c}$$

in which $F^c_n = \frac{1}{2}(\boldsymbol{\theta}^0 \pm \mathrm{i}\boldsymbol{\phi}^0).\mathbf{F}_n$.

Explicit forms for $\mathcal{F}_{nn'}$ and $\mathcal{G}_{mm'}$ in a particular case are given in §5.

(ii) *Discussion of the result, equation* (32)

Consider first the case when the polarization of the exciting light allows excitation to only one state $|n\rangle$ of the excited level, so that $n' = n$. The result (32) shows that the light intensity is modulated at frequencies $|m-m'|\,\omega_0$. The angular dependence of the emitted light is contained in the elements $\mathcal{G}_{mm'}$ of the emission matrix. The rotation matrix elements give the variation of intensity with field and frequency. They all show some type of resonant behaviour near $\delta = 0$, i.e. when $H = H_0 = \omega_0/\gamma$. The term $\Gamma/(\Gamma+\mathrm{i}x)$, which reduces to $\Gamma/\{\Gamma+\mathrm{i}(\mu-\mu')\,p\}$, also shows resonant behaviour near $\delta = 0$ unless $\mu = \mu'$, in which case it is independent of H. The terms of zero-frequency ($m = m'$) sum to give the well known Brossel–Bitter resonance (Brossel & Bitter 1952).

The more general case when more than one of the $|n\rangle$ are simultaneously excited shows additional features which have been observed in the experiments, namely, modulation at frequencies higher than the maximum value of $|m-m'|\,\omega_0$, and resonance effects at frequencies other than H_0. The possible modulation frequencies are now $|m-m'-n+n'|\,\omega_0$. The extra resonance effects are seen in the behaviour of the term $\Gamma/(\Gamma+\mathrm{i}x)$ when $x = 0$, i.e. when $(\mu-\mu')\,p = (n'-n)\,\omega_0$. In the case of the $^3P_1-{}^1S_0$ transition, modulation up to the fourth harmonic is present, and resonances occur when $H = 0$, $\frac{1}{2}H_0$, $\frac{3}{2}H_0$, $2H_0$ and $3H_0$. Not all of these may be strong enough to be easily observable.

5. APPLICATION TO THE TRANSITION $6^3P_1 - 6^1S_0$ IN MERCURY

Atoms in the ground level 6^1S_0 are excited by light of wavelength 2537 Å to the level 6^3P_1, whose states $|m_J = 0, \pm 1\rangle$ are connected by the radio-frequency field. The expression (32) for the intensity of the fluorescent light is most readily understood by separate attention to the three parts of the process.

(i a) *Excitation*

The coefficients F_n for the case of incident light passing through a linear polarizer specified by the unit vector $\mathbf{e}_i^0$ are given by $F_n = \mathbf{e}_i^0 . \langle n | \mathbf{P} | g \rangle$. Using the matrix elements for $\langle n | \mathbf{P} | g \rangle$ given by Condon & Shortley (1951, p. 53), and equation (8) we obtain

$$F_{\pm 1} = 2^{-\frac{1}{2}} P (\cos \alpha_i \cos \theta_i \mp \mathrm{i} \sin \alpha_i) \exp (\mp \mathrm{i} \phi_i), \Big\}$$
$$F_0 = - P (\cos \alpha_i \sin \theta_i), \qquad\qquad\qquad \Big\} \tag{34}$$

where $P = \langle 1 | P | 0 \rangle$.

For the particular case of light incident along the x-axis, polarized so that the electric vector makes an angle α_i with the direction of the field, the excitation matrix becomes

$$\mathscr{F}_{nn'} = |P|^2 \begin{pmatrix} \frac{1}{2} \sin^2 \alpha_i & -2^{-\frac{1}{2}} \mathrm{i} \sin \alpha_i \cos \alpha_i & \frac{1}{2} \sin^2 \alpha_i \\ 2^{-\frac{1}{2}} \mathrm{i} \sin \alpha_i \cos \alpha_i & \cos^2 \alpha_i & 2^{-\frac{1}{2}} \mathrm{i} \sin \alpha_i \cos \alpha_i \\ \frac{1}{2} \sin^2 \alpha_i & -2^{-\frac{1}{2}} \mathrm{i} \sin \alpha_i \cos \alpha_i & \frac{1}{2} \sin^2 \alpha_i \end{pmatrix}. \tag{35a}$$

For the case of unpolarized light, a matrix obtained by replacing α_i by $\alpha_i + \frac{1}{2}\pi$ must be added to the above. The excitation matrix is then

$$\mathscr{F}_{nn'}^u = |P|^2 \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}. \tag{35b}$$

(i b) *The mixing of states*

The effect of the radio-frequency magnetic field in producing a coherent mixture of the states $|m\rangle$ is contained in the products

$$\langle m | \mu \rangle \langle \mu | n \rangle \langle n' | \mu' \rangle \langle \mu' | m' \rangle.$$

The rotation matrix elements, for $J = 1$, are

$$\langle m | \mu \rangle = \begin{pmatrix} \cos^2 \frac{1}{2}\beta & -\sqrt{2} \sin \frac{1}{2}\beta \cos \frac{1}{2}\beta & \sin^2 \frac{1}{2}\beta \\ \sqrt{2} \sin \frac{1}{2}\beta \cos \frac{1}{2}\beta & \cos^2 \frac{1}{2}\beta - \sin^2 \frac{1}{2}\beta & -\sqrt{2} \sin \frac{1}{2}\beta \cos \frac{1}{2}\beta \\ \sin^2 \frac{1}{2}\beta & \sqrt{2} \sin \frac{1}{2}\beta \cos \frac{1}{2}\beta & \cos^2 \frac{1}{2}\beta \end{pmatrix} \tag{36}$$

in which β is defined in §3 (figure 1 (c)). The elements $\langle \mu | m \rangle$ are obtained by transposition of rows and columns.

The variation of these matrix elements, and of the factor $\Gamma/(\Gamma + \mathrm{i}x)$, with H, gives rise to resonances in the steady and modulated components of the fluorescent radiation.

(i c) *Emission*

The angular distribution of the fluorescent light is determined by the emission matrix $\mathscr{G}_{mm'}$. If no analyzer is used, $\mathscr{G}^u_{mm'} = \mathbf{G}^*_m . \mathbf{G}_{m'}$ with

$$\left. \begin{aligned} \mathbf{G}_{\pm 1} &= \mp 2^{-\frac{1}{2}} P(\boldsymbol{\theta}^0 \cos\theta \mp \mathrm{i}\boldsymbol{\phi}^0)\, \mathrm{e}^{\mp \mathrm{i}\phi}, \\ \mathbf{G}_0 &= -P\boldsymbol{\theta}^0 \sin\theta. \end{aligned} \right\} \tag{37}$$

For observation in the direction θ, ϕ the emission matrix becomes

$$\mathscr{G}^u_{mm'} = |P|^2 \begin{pmatrix} \frac{1}{2}(\cos^2\theta + 1) & 2^{-\frac{1}{2}}\sin\theta\cos\theta\, \mathrm{e}^{\mathrm{i}\phi} & \frac{1}{2}\sin^2\theta\, \mathrm{e}^{\mathrm{i}2\phi} \\ 2^{-\frac{1}{2}}\sin\theta\cos\theta\, \mathrm{e}^{-\mathrm{i}\phi} & \sin^2\theta & -2^{-\frac{1}{2}}\sin\theta\cos\theta\, \mathrm{e}^{\mathrm{i}\phi} \\ \frac{1}{2}\sin^2\theta\, \mathrm{e}^{-\mathrm{i}2\phi} & -2^{-\frac{1}{2}}\sin\theta\cos\theta\, \mathrm{e}^{-\mathrm{i}\phi} & \frac{1}{2}(\cos^2\theta + 1) \end{pmatrix}. \tag{38}$$

If an analyzer is used to select the electric vector at angle α, the elements of the emission matrix are $\mathscr{G}_{mm'} = G^*_m G_{m'}$, where the $G_m = \mathbf{e}^0 . \mathbf{G}_m$ are given by equations like (34).

(ii) *Excitation to a single state*

The terms of equation (32) will be evaluated for the particular case of excitation to the state $|0\rangle$ exclusively (light incident along the x-axis, $\alpha_i = 0$). Writing I_0 for the accumulation of constants, we find

$$\begin{aligned} I = I_0 \frac{N}{\Gamma} \big[&\sin^2\theta + (\cos^2\theta - \tfrac{1}{2}\sin^2\theta)\, 2A \\ &- \sin\theta\cos\theta\,\{ B\cos(\omega_0 t - \phi) + C\sin(\omega_0 t - \phi)\} \\ &- \sin^2\theta\,\{ D\cos(2\omega_0 t - 2\phi) + E\sin(2\omega t - 2\phi)\} \big] \end{aligned} \tag{39}$$

in which

$$A = \frac{b^2(4\delta^2 + b^2 + \Gamma^2)}{(\delta^2 + b^2 + \Gamma^2)(4\delta^2 + 4b^2 + \Gamma^2)},$$

$$B = \frac{2b\delta(4\delta^2 - 2b^2 + \Gamma^2)}{(\delta^2 + b^2 + \Gamma^2)(4\delta^2 + 4b^2 + \Gamma^2)},$$

$$C = \frac{2b\Gamma(4\delta^2 + b^2 + \Gamma^2)}{(\delta^2 + b^2 + \Gamma^2)(4\delta^2 + 4b^2 + \Gamma^2)},$$

$$D = \frac{b^2(2\delta^2 - b^2 - \Gamma^2)}{(\delta^2 + b^2 + \Gamma^2)(4\delta^2 + 4b^2 + \Gamma^2)},$$

$$E = \frac{3b^2\Gamma\delta}{(\delta^2 + b^2 + \Gamma^2)(4\delta^2 + 4b^2 + \Gamma^2)}.$$

The quantity A determines the variation of the unmodulated component of the fluorescent light as one alters H (or ω_0); this displays a resonance when

$$\delta = \omega - \omega_0 = 0,$$

i.e. at $H = H_0$. The variation is exactly that described by Brossel & Bitter (1952).

The intensity is also modulated at the first and second harmonics of the applied radio-frequency, the variation of amplitude and phase of the modulations being

described by the quantities B, C and D, E, respectively. The quantities B and C bear a striking resemblance to the solutions of the Bloch equations, which lends support to the belief that the modulation may also be described by the phenomenological approach of Bell & Bloom (1957). It is to be noticed that the phase of the modulations (with respect to that of the oscillating field) varies as one goes through resonance, and is a function of the azimuth angle ϕ.

The variations have received experimental confirmation in work which has been briefly reported (Dodd *et al.* 1959) and which is to be more fully described in a later paper. In particular, the variations with angle of observation, and of polarizer and analyzer have been confirmed.

(iii) *Excitation to a mixture of states*

As a further example we show how, and under what conditions, resonances can occur near the fields $H = \frac{1}{2}H_0$ and $\frac{3}{2}H_0$.

The general expression for the intensity (equation (32)) is a formidable one, but it is possible to extract from the summations those terms which have a resonance in a certain region of magnetic field. Resonances occur when the quantity $x = (\mu - \mu')p + (n - n')\omega_0$ in the equation passes through zero. For the particular terms in which $n - n' = +1$, $\mu - \mu' = -2$, and $n - n' = -1$, $\mu - \mu' = +2$, this leads to the condition $2p = \omega_0$ for resonance. Expressed in terms of fields the condition is

$$H = H_0 \pm \tfrac{1}{2}H_0(1 - 4H_1^2/H_0^2)^{\frac{1}{2}}. \tag{40}$$

If H_1 is not too large this gives $H \approx \frac{1}{2}H_0$ and $H \approx \frac{3}{2}H_0$ for the resonances. As H_1 approaches the value $\frac{1}{2}H_0$, both resonances move towards H_0.

The frequencies of modulation of the intensity at these resonances are the possible values of $|m - m' - n + n'|\,\omega_0$. Since $m - m'$ can take all values from zero to ± 2 (and recalling that we have selected those terms for which $n - n' = \pm 1$) we find terms in unmodulated, fundamental, second- and third-harmonic components of the intensity. The strengths of the resonances of these various components are not all the same; they depend on some power of H_1/H_0. The strongest resonances predicted (for small H_1) are those of the unmodulated and fundamental components which occur near $\frac{1}{2}H_0$. These have been observed. Resonances near $\frac{1}{2}H_0$ and $\frac{3}{2}H_0$ have also been observed in the light modulated at the second and third harmonics. The third harmonic resonance at $\frac{3}{2}H_0$ is stronger than that at $\frac{1}{2}H_0$ as predicted by the theory.

A necessary condition for the production of these resonances at $\frac{1}{2}H_0$ and $\frac{3}{2}H_0$ is the excitation of a mixture of states $|n\rangle$ between which n differs by unity. For light incident along the x-axis, this implies that plane polarized light must be polarized obliquely to the magnetic field. This accords with the appearance of the factor $\sin \alpha_i \cos \alpha_i$ which is common to all the terms at present under consideration. The necessity of oblique polarization has been confirmed by experiment.

Among the other terms in equation (32) are some which give rise to resonances at zero field, at $2H_0$ and at $3H_0$. Modulations up to the fourth harmonic are found at these fields. Systematic experimental study of the higher modulations has not yet been undertaken.

6. FREQUENCY DIAGRAM

In the course of these studies we have found it useful to develop a frequency diagram for the excited state $J = 1$ to represent its structure under the simultaneous application of a steady field along Oz and rotating field in the xy plane. A diagram of this type for $J = \frac{1}{2}$ was drawn by Pryce (1950). The frequency diagram is simply a generalization, for the case when the Hamiltonian function is time-dependent, of the normal term diagram. To each state, in the normal case, there corresponds one and only one frequency. When the Hamiltonian is periodic in time there may be more than one. The representation of radiation damping by broadened energy levels is a familiar example of this generalized term diagram.
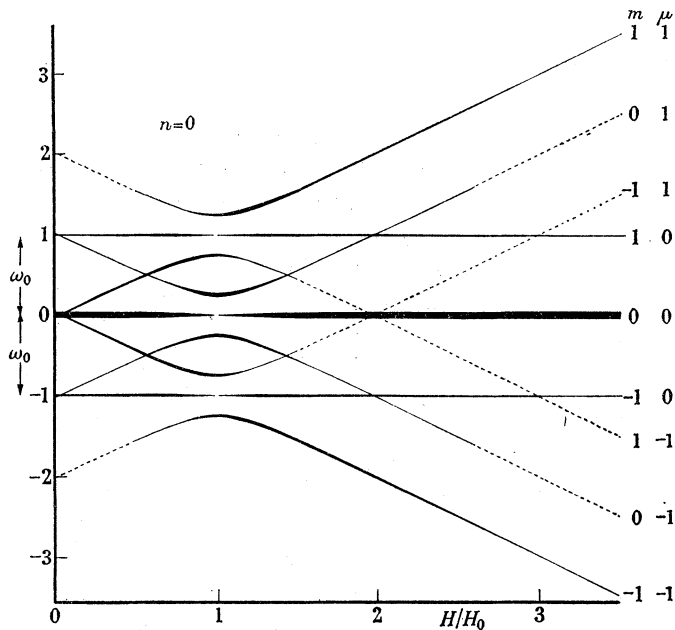

FIGURE 2. The frequency diagram.

The terms in equation (20) which represent the excited state contain, after separating the factor $\exp\{-i(k_0 - \frac{1}{2}i\Gamma)\}$, oscillating terms of frequency $(m\omega_0 \pm \mu p)$. For example, when $n = 0$ the probability amplitudes of the states $|1\rangle$, $|0\rangle$, and $|-1\rangle$ are in the ratio

$$[2sc^3 \exp\{-i(\omega_0 + p)\,t'\} \quad -2sc(c^2 - s^2)\exp(-i\omega_0 t')$$
$$-2s^3c \exp\{-i(\omega_0 - p)\,t'\}]\exp(-i\omega_0 t_0)$$

$$: [2s^2c^2\exp(-ipt') \quad +(c^2 - s^2)^2$$
$$+2s^2c^2\exp\{-i(-p)\,t'\}]$$

$$: [2s^3c \exp\{-i(-\omega_0 + p)\,t'\} + 2sc(c^2 - s^2)\exp\{-i(-\omega_0)\,t'\}$$
$$-2sc^3 \exp\{-i(-\omega_0 - p)\,t'\}]\exp\{-i(-\omega_0)t_0\}$$

in which $s = \sin\frac{1}{2}\beta$, $c = \cos\frac{1}{2}\beta$ and $t' = t - t_0$. The frequency diagram associated with the excited level is shown in figure 2.

The interpretation of the diagram is facilitated by recalling how the expansion was obtained. The states $|m\rangle$ were defined with reference to a laboratory co-ordinate system in which a steady magnetic field $\mathbf{H}$ is applied along Oz. The frequencies of the $|m\rangle$, $(k_0+)m\gamma H$, are shown in figure 3 (a) as functions of H.
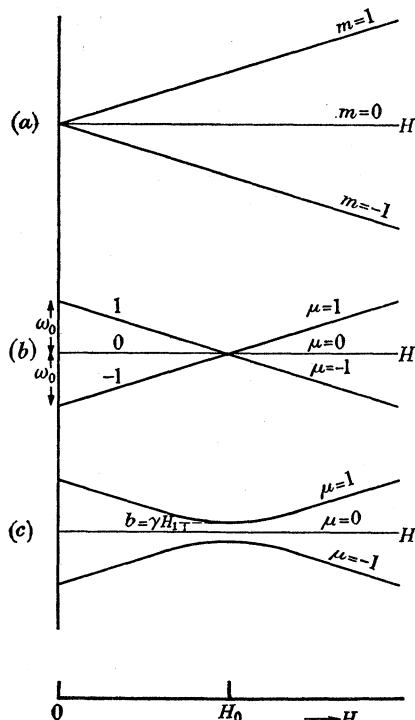

FIGURE 3. Precessional frequencies, f, as functions of H. (a) Laboratory co-ordinate system. $f = m\gamma H$ about $\mathbf{H}$. (b) Rotating co-ordinate system. No radio-frequency field. $f = \mu\gamma|H - H_0|$ about $\mathbf{H}_{\text{eff.}}$. (c) Rotating co-ordinate system. Radio-frequency field applied. $f = \mu\gamma[(H - H_0)^2 + H_1^2]^{\frac{1}{2}}$ about $\mathbf{H}_{\text{eff.}}$.

The transformation was then made to a co-ordinate system rotating about Oz with angular velocity ω_0, in which system the frequencies of the $|m\rangle$ are decreased by $m\omega_0$. In anticipation of the subsequent addition of the field $\mathbf{H}_1$, it was found convenient to quantize with reference to an axis Oz', parallel to the effective field in the rotating system. The quantum numbers μ label the states with reference to Oz'. Before $\mathbf{H}_1$ is added the effective field is always either parallel or anti-parallel to Oz, according as H is greater or less than ω_0/γ. The state $|\mu = 1\rangle$ always has a higher frequency than $|\mu = 0\rangle$ or $|\mu = -1\rangle$ and lies above them in figure 3 (b) for all values of H.

The field $\mathbf{H}_1$ was then added. In the rotating system $\mathbf{H}_1$ is steady, along Ox'. The effective field, $[(\mathbf{H} - \omega_0/\gamma) + \mathbf{H}_1]$ now makes an angle β with Oz. The Larmor precessional frequencies, μp, about $\mathbf{H}_{\text{eff.}}$, are shown in figure 3 (c). p is often termed the 'flipping frequency'.

Since the $|\mu\rangle$ are linear superpositions of the $|m\rangle$ each of the $|m\rangle$ is fractionally associated with each level in figure 3 (c). Thus, in the return to the laboratory system,

when the frequency of each state $|m\rangle$ is increased by $m\omega_0$, the diagram of figure 2 is obtained, in which the number of frequency levels is $(2J+1)^2$.

The thicknesses of the levels in figure 2 indicate the relative magnitudes of the coefficients of each frequency term in the expansion. The magnitudes used are those appropriate to $n = 0$. While they give some representation of relative probabilities, they are neither probability amplitudes nor true probabilities. Within a given $|m\rangle$, the coefficients give relative probabilities for the three frequencies μp. The sum of these probabilities is the relative probability amplitude of the state $|m\rangle$.

Transitions induced by the rotating magnetic field must be interpreted on the diagram in the following manner: absorption or emission of a radio-frequency photon corresponds to a change of frequency by ω_0, i.e. a jump between two parallel curves. In this transition m changes by ± 1, but μ remains unchanged (as it must, since it labels the eigenstates in the rotating co-ordinate system, in which the Hamiltonian is independent of time).

Use of the diagram

One can see immediately from the diagram that the Brossel–Bitter 'double resonance' curve is double-peaked. The thicknesses of the levels which represent the states $|m = \pm 1\rangle$ are greatest in the region of H_0, but have their maxima, at two values of the field slightly higher and lower than H_0. As H_1 is reduced the curves for $\mu = \pm 1$ approach their asymptotes as in figure 3(b), and the positions of maximum thickness move closer to the centre. Not indicated in figure 2 is the natural width of the levels due to radiative decay. Thus, when H_1 becomes small, the resolution of the double peak is lost in the natural width of the resonance. Figure 2 is drawn for a ratio $H_1/H_0 = \frac{1}{4}$, which is higher than is used for most experiments of the double resonance type, but corresponds to the conditions used in the experiments of Dodd *et. al.* (1959).

Questions concerning the coherence between different states, and possibilities of light modulation, may also be answered by reference to the diagram. Let us suppose that the exciting light is steady, and of wide spectral range. In a Fourier expansion of the amplitude of the light vector, the phases of the components $\mathbf{E}(k)$ will be random, corresponding to the random positions and motion of the radiating atoms in the source. Hence the optical perturbation will excite incoherently states which are at different levels in the frequency diagram (the word 'state' here is not used in its ordinary sense). The radio-frequency perturbation, however, links states of different m but the same μ. Thus, if the optical perturbation excites $(m, \mu) = (0, 0)$, then the radio-frequency perturbation will establish coherence between $(1, 0)$, $(0, 0)$ and $(-1, 0)$, whatever the value of the field H. The frequency differences which are found between the coherent levels (ω_0 and $2\omega_0$ in this case) are found as modulation frequencies in the fluorescent radiation. The depth of modulation will depend on those parameters (H, H_1, etc.) which govern the relative 'weights' of the coherent states.

Light of the particular polarization which excited $(0, 0)$ will excite $(0, 1)$ and $(0, -1)$ also, but since the frequencies associated with these states are different, they are excited by different components of the optical field, and therefore incoherent with

respect to the states $\mu = 0$. Frequency differences between incoherent levels do not appear in the modulation of the fluorescent radiation.

An important exception to the rule that levels of different μ are incoherent occurs when such levels intersect, for then they may be excited by the same component of the optical field. In this case, provided the excitation has taken place from some common initial level, coherence obtains between the intersecting levels and all others of the same values of μ. The consequences of this coherence were examined analytically in §5(iii). The diagram allows similar conclusions to be drawn more directly. Consider, for example, the relative positions of the levels when $H \approx \frac{1}{2}H_0$. Coherence obtains between $(0, 1)$ and $(1, -1)$ because of the intersection when they are both excited from the same ground level. Further, by virtue of the radio-frequency perturbation, all other levels which have $\mu = 1$ or -1 are coherent with the intersecting pair. Only the levels $\mu = 0$ remain incoherent. The possible frequency differences between the coherent levels are 0, ω_0, $2\omega_0$, $3\omega_0$; consequently the fluorescent light is modulated at these frequencies. The phenomenon is confined to the region of intersection since the coherence between $(0, 1)$ and $(1, -1)$ is lost as one moves away.

One can immediately see, from a study of figure 2, at what fields are to be found the resonances associated with intersections, and at what frequencies the light will be modulated. In addition to the intersections near $\frac{1}{2}H_0$ which we have discussed, there exist intersections near $\frac{3}{2}H_0$ with possibilities for modulation up to, but not exceeding the third harmonic, and further intersections near the fields 0, $2H_0$ and $3H_0$. The possibilities for modulation here include the fourth harmonic.

The association of intersections in the frequency diagram with abnormal intensities in the fluorescent light relates this work with that of Hanle (1924, 1925) on the polarization of resonance radiation in low fields, and with that of Colegrove, Franken, Lewis & Sands (1959) on intensity changes in the region of intersecting energy levels. All these phenomena are completely described by equation (32), with ω (i.e. H) taking small positive and negative values in the neighbourhood of $\omega = 0$, and with H_1 and $\omega_0 = 0$. It is to be noticed that the half-intensity widths of the resonances which are associated with intersecting levels both in modulated and in unmodulated light, are determined by the natural widths of the levels. This contrasts with the resonances which occur at H_0 for which the half-intensity widths are determined by the magnitude of the radio-frequency field if that is sufficiently strong. These predictions are borne out by the experiments.

Finally, it is to be noticed that further possibilities for coherence arise if the exciting radiation is modulated or pulsed, for coherence then resides in the optical perturbation itself. The consequences of this can be deduced qualitatively from a frequency diagram such as figure 2 if a radio-frequency field (or other periodic perturbation of sharp frequency) is acting on the scattering material, or from an ordinary term diagram if there is no such field.

us to study his work before publication, to Professor W. E. Lamb and Dr R. J. Blin-Stoyle for criticism of early drafts of this paper, and to a referee for his constructive suggestions, in particular for his suggestion of the use of the operator U. We owe to Professor Barrat the suggestion that resonances at fields other than H_0 may be due to coherent excitation into states of different polarization.

References

Bell, W. & Bloom, A. 1957 *Phys. Rev.* **107**, 1559.

Born, M. & Wolf, E. 1959 *Principles of optics*. London: Pergamon Press.

Brossel, J. & Bitter, F. 1952 *Phys. Rev.* **86**, 308.

Colegrove, F. D., Franken, P. A., Lewis, R. R. & Sands, R. H. 1959 *Phys. Rev. Lett.* **3**, 420.

Condon, E. U. & Shortley, G. H. 1951 *The theory of atomic spectra*. Cambridge University Press.

Dehmelt, H. G. 1957 *Phys. Rev.* **105**, 1924.

Dodd, J. N., Fox, W. N., Series, G. W. & Taylor, M. J. 1959 *Proc. Phys. Soc.* **74**, 789.

Hanle, W. 1924 *Z. Phys.* **30**, 93.

Hanle, W. 1925 *Egebn. exakt. Naturw.* **4**, 214.

Majorana, E. 1932 *Nuovo Cim.* **9**, 43.

Pryce, M. H. L. 1950 *Phys. Rev.* **77**, 136.

Rabi, I. I., Ramsey, N. F. & Schwinger, J. 1954 *Rev. Mod. Phys.* **26**, 167.

Ramsey, N. F. 1956 *Molecular beams*. Oxford University Press.

Rose, M. E. 1957 *Elementary theory of angular momentum*. New York: John Wiley and Sons, Inc.

Salwen, H. 1955 *Phys. Rev.* **99**, 1274.