Proposal for Measuring Lamb Shifts by the Study of Modulated, Fluorescent Light

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A method is proposed for measuring the interval between two atomic energy levels of different parity. The method is related to optical radio-frequency double resonance and level-crossing experiments in that the behavior of atoms in excited states is deduced from observations of the fluorescent light. In contrast with the oscillating electric field ordinarily used to stimulate transitions between states of opposite parity, a small, static electric field is required. The rate at which atoms are excited is required to be modulated; consequently, the fluorescent light will be modulated. The amplitude of modulation will depend on the parameters. A general expression is derived. Two cases are of particular interest: (1) A resonance effect is predicted if the frequency of modulation matches the interval between the perturbed levels. This effect could best be studied for frequencies much greater than the combined natural widths of the levels. (2) For frequencies smaller than the natural width, a level-crossing effect is predicted whose peak occurs at the point of intersection of the unperturbed levels. The method might be applied to measure intervals between the 2s and 2p levels in hydrogen. Estimates are given of the required fields and frequencies.

1. INTRODUCTION

IN recent years a number of new techniques have been developed for studying the intervals between close-lying energy levels in excited atoms.[1] The techniques have in common the measurement of the intensity of the radiation emitted when the atoms decay, but the fundamental basis of the experiments is different according to whether the states concerned are members of a Zeeman or hyperfine multiplet, in which case they are of the same parity and decay at the same rate, or whether they are of different parity, and decay at different rates, as, for example, the $2\,^2S_{1/2}$ and $2\,^2P_{1/2}$ states in hydrogen. In both cases the application of oscillating fields, capable of inducing transitions between the states of interest, causes changes in the emitted radiation. In the former case the character of the transitions is magnetic dipole. The effect of these transitions is primarily to alter the spatial distribution of the radiation; the spectral distribution changes very little. In the latter case the transitions are electric dipole. The change of parity which this implies requires that the atom must decay to an entirely different term, so that the spectral distribution of the radiation changes profoundly.

In the case when the states are members of a multiplet, changes in the spatial distribution of the light occur also when the energy levels are degenerate, a situation which is frequently found in the intermediate-field region of the Zeeman effect in hyperfine structure. (In fact, the effect was discovered in connection with the ordinary triplet structure in helium.[2]) The method of locating these level crossings by measuring the intensity of the fluorescent radiation in some particular direction, as a function of magnetic field, is a very elegant method of studying hyperfine or multiplet structure, partly on account of its simplicity, and partly because the precision with which the points of intersection may be determined is limited only by the natural width of the energy levels.

The level-crossing technique cannot be applied when the degenerate levels are an isolated pair of different parity, since the states concerned cannot then be transformed into one another by rotations. A superficial analysis might suggest that the mixing of states provided by a static electric field would allow level-crossing effects to be detected, but on examination it becomes clear that the intensity of the fluorescent radiation must be independent of the degree of mixing (cf. Sec. 5).

Rose and Carovillano[3] considered the possibilities of detecting level crossings in the $n = 2$ states of hydrogen, with a view to determining the Lamb shift. The p-p intersections, which can in principle be located by the technique we have mentioned, give no information about the Lamb shift. The s-p intersections can in this case be located by the level-crossing technique by taking advantage of the proximity of other p states, for a strong electric field can mix into the s state some fraction of a nearby p state and endow it with sufficient p character to make the experiment feasible. However, if the field is to be sufficiently strong to achieve this mixing, the perturbation of energy levels will be such that the position of the level crossing becomes quite insensitive to the value of the Lamb shift.

The purpose of this paper is to propose a type of experiment which would allow the location of crossing points between energy levels of different parity, and thus provide an alternative method for measuring the Lamb shift. The basis of the method is to exploit the possibility of temporal, rather than spatial redistribution of resonance fluorescence. We propose to consider changes in the amplitude of modulation of the fluorescent light when the rate of excitation of the atoms (either by light or by electron impact) is modulated. A small, static electric field is required to mix the

[1] J. Brossel and F. Bitter, Phys. Rev. 86, 308 (1952); W. E. Lamb and M. Skinner, *ibid.* 78, 539 (1950). For a review of later developments, see G. W. Series, Rept. Progr. Phys. 22, 280 (1959).

[2] F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters 3, 420 (1959).

[3] M. E. Rose and R. L. Carovillano, Phys. Rev. 122, 1185 (1961).

states, but the requirement of Rose and Carovillano for an optimum effect, that the field should be parallel to the axis of quantization, does not concern us here. The argument will hold for any pair of states between which a perturbation can be established by a suitably oriented electric field. One variant of the experiment makes use of the fact that the degree of mixing provided by a field of constant magnitude depends on the separation of the energy levels; another makes use of the resonance effects which are to be expected when the frequency of modulation matches the interval between the perturbed levels. Resonances of this sort have been studied when the states concerned were members of a Zeeman multiplet.[4]

We shall analyze the case of an isolated pair of excited energy levels belonging to states of opposite parity, having in mind any pair of intersecting s and p levels in hydrogen-like atoms. The presence of other fine structure levels will not substantially affect the argument. We shall consider first the effect of an electric field on the excited states and energy levels, and calculate the intensity of the light which would be emitted from an atom instantaneously excited into the p state. We shall show that this should be modulated. We shall then show that the intensity of the fluorescence from atoms excited to the p state at a uniform rate is unmodulated, independent of the electric field, and independent of the proximity of the s state. Finally, we shall show that, when the rate of excitation is modulated, the amplitude of modulation of the fluorescent light *does* depend on the interval between the s and p levels.

2. TIME-DEPENDENT WAVE FUNCTION OF THE EXCITED ATOM

Consider the effect of a perturbing electric field on an atom whose eigenstates $|a\rangle$, $|b\rangle$ of the Hamiltonian $\mathcal{3C}_0$ have eigenvalues $\hbar k_a$, $\hbar k_b$. Let $\hbar V$ be the perturbation Hamiltonian. We shall treat radiative decay by introducing a damping Hamiltonian $\mathcal{3C}_D$ whose matrix is diagonal, with elements 0 for $|a\rangle$ and $-i\hbar\gamma/2$ for $|b\rangle$, that is to say, the state $|a\rangle$ is supposed to be non-radiative. V is independent of time, as are $\mathcal{3C}_0$ and $\mathcal{3C}_D$. (See Fig. 1.)

Let $|t\rangle$ be the state of the atom at time t. We need to solve the equation of motion

$$i\hbar(d|t\rangle/dt) = (\mathcal{3C}_0 + \mathcal{3C}_D + \hbar V)|t\rangle. \quad (1)$$

Expanding $|t\rangle$ in eigenstates of $\mathcal{3C}_0$ in the interaction representation:

$$|t\rangle = a(t)\exp(-ik_a t)|a\rangle + b(t)\exp(-ik_b t)|b\rangle, \quad (2)$$

substituting (2) in (1), and using the orthogonal

[4] E. B. Aleksandrov, Opt. i Spektroskopiya 14, 436 (1963) [English transl.: Opt. Spectry. (USSR) 14, 232 (1963)]. A. Corney and G. W. Series, Proc. Phys. Soc. (London) 83, 207, 213, and 331 (1964). O. Nedelec and J. C. Pebay-Peyroula, Compt. Rend. 254, 1951 (1962).
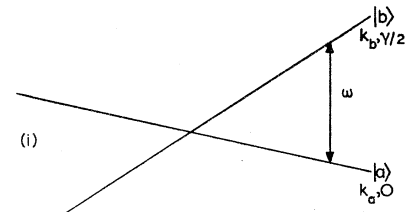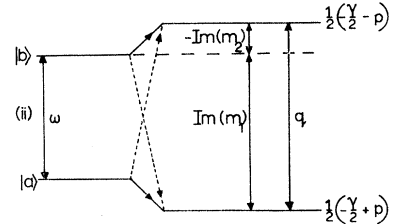

FIG. 1. (i) The unperturbed system. (ii) Effect of the perturbation.

property of $|a\rangle$ and $|b\rangle$, we obtain two equations from which the differential equation for $b(t)$ may be obtained:

$$\ddot{b} + \dot{b}(\gamma/2 - i\omega) + b(|V|^2 - i\omega\gamma/2) = 0, \quad (3)$$

where $\omega = k_b - k_a$.

The general solution

$$b = B_1 \exp(m_1 t) + B_2 \exp(m_2 t) \quad (4)$$

satisfies (3) with

$$m_1 = \tfrac{1}{2}\{(-\gamma/2 + p) + i(\omega + q)\}$$

and

$$m_2 = \tfrac{1}{2}\{(-\gamma/2 - p) + i(\omega - q)\}, \quad (5)$$

where

$$p = \{\tfrac{1}{2}\{(\gamma^2/4 - \omega^2 - 4|V|^2) + [(\gamma^2/4 + \omega^2 + 4|V|^2)^2 - 4|V|^2\gamma^2]^{1/2}\}\}^{1/2},$$

$$q = \{\tfrac{1}{2}\{-(\gamma^2/4 - \omega^2 - 4|V|^2) + [(\gamma^2/4 + \omega^2 + 4|V|^2)^2 - 4|V|^2\gamma^2]^{1/2}\}\}^{1/2},$$

and

$$pq = \gamma\omega/2. \quad (6)$$

The two terms in the probability amplitude of $|b\rangle$,

$$\{B_1 \exp(m_1 t) + B_2 \exp(m_2 t)\}\exp(-ik_b t),$$

indicate that the atom can exist in state $|b\rangle$ at either of two levels which differ in frequency by $\text{Im}(m_1 - m_2) = q$, and with decay constants $\text{Re}(m_1) = \tfrac{1}{2}(-\gamma/2 + p)$ and $\text{Re}(m_2) = \tfrac{1}{2}(-\gamma/2 - p)$, respectively. Similarly, the solution for $a(t)$ expressed in the form $a(t) = A_1 \exp(n_1 t) + A_2 \exp(n_2 t)$ yields

$$n_1 = \tfrac{1}{2}\{(-\gamma/2 + p) - i(\omega - q)\}$$

and

$$n_2 = \tfrac{1}{2}\{(-\gamma/2 - p) - i(\omega + q)\}.$$

The exponents $(n_1 - ik_a)t$, $(n_2 - ik_a)t$ in the probability amplitude of $|a\rangle$ are identical with those in the probability amplitude of $|b\rangle$. In deriving this familiar
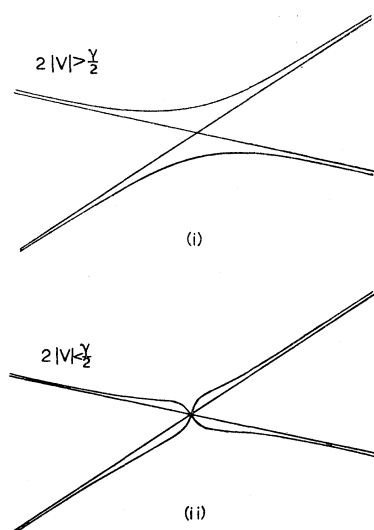
FIG. 2. Effect of the perturbation in the region of the level crossing.

(i) $2|V| > \gamma/2$;
(ii) $2|V| < \gamma/2$.

result, we wish to emphasize that if an atom is either in state $|a\rangle$ or in state $|b\rangle$, its wave function contains two frequencies. States $|a\rangle$ and $|b\rangle$ share the same energy levels and the same decay constants, but the probability amplitudes depend on the initial conditions and on the time.

Solutions corresponding to (5) were obtained by Lamb[5] who pointed out an interesting feature of the result in the region of the level crossing. When $2|V| > \gamma/2$, the energy levels repel one another, as in Fig. 2(i), but when $2|V| < \gamma/2$, the levels continue to cross at the same point where they would have crossed in the absence of the perturbation, as in Fig. 2(ii). In case (i), the states are completely mixed at the crossing point, but in case (ii) the mixing is only partial. The variation of the mixing in the region of the crossing point is the basis of one form of the experiment we are proposing.

The solution (4) is completed by finding B_1 and B_2 for given initial conditions. The conditions $b=1$ and $a=0$ at $t=0$ lead to

$$B_1 = (\gamma/2 + m_2)/(m_2 - m_1),$$
$$B_2 = (\gamma/2 + m_1)/(m_1 - m_2), \qquad (7)$$

and

$$A_1 = -A_2 = iV_{ab}/(m_2 - m_1).$$

We are now in a position to consider the emission of light by an excited atom.

3. THE EMISSION LIGHT

We consider the decay from the excited state to a lower state $|g\rangle$. We suppose that matrix elements of the electric dipole exist between $|b\rangle$ and $|g\rangle$, but not between $|a\rangle$ and $|g\rangle$. The intensity of the component of radiation whose electric vector is parallel to the unit vector $\mathbf{e}^0$ is proportional to

$$|\langle g|\mathbf{e}^0 \cdot \mathbf{P}|t\rangle|^2.$$

[5] W. E. Lamb, Phys. Rev. 85, 259 (1952).

Expanding $|t\rangle$, we find that $I(t,0)$, the intensity at time t from atoms excited at $t=0$, is proportional to $|b(t)|^2$, where the constant of proportionality depends on the matrix element $|\langle g|\mathbf{e}^0 \cdot \mathbf{P}|b\rangle|^2$, the direction in which the light is observed, and other constants which need not concern us.

Using Eq. (4), with m_1 and m_2 given by (5) and B_1 and B_2 by (7), we find

$$I(t,0) \propto c_1 \exp(-\gamma/2 + p)t + c_2 \exp(-\gamma/2 - p)t$$
$$+ 2(\alpha \cos qt - \beta \sin qt)\exp(-\gamma/2)t, \quad (8)$$

where

$$c_1 = |B_1|^2 = \{(\gamma/2 - p)^2 + (\omega - q)^2\}/4(p^2 + q^2),$$
$$c_2 = |B_2|^2 = \{(\gamma/2 + p)^2 + (\omega + q)^2\}/4(p^2 + q^2), \quad (9)$$

and

$$(\alpha + i\beta) = B_1 B_2^* = \{(p^2 - \gamma^2/4 + q^2 - \omega^2)$$
$$+ i(q\gamma - 2p\omega)\}/4(p^2 + q^2).$$

Equation (8) predicts that the radiation from an assembly of atoms excited simultaneously and instantaneously to the state $|b\rangle$ should consist of two components exponentially damped at different rates, and a component modulated at the frequency q damped at half the unperturbed rate of radiation from $|b\rangle$. The modulation arises from the fact that the atom can exist in the state $|b\rangle$ at two different levels of frequency. It is to be noticed that q is the interval between the perturbed, not the unperturbed levels.

4. THE PROCESS OF EXCITATION

We suppose that the atoms are excited to $|b\rangle$ either by light of spectral range Δ much greater than q, or by electron impact. Coherence of phase in the process of excitation is lost in a time $\sim 1/\Delta$ in the first case, or within the interaction time in the second. Provided these times are much smaller than the mean lifetime of the excited atom, we may treat the process of excitation as a rate process. The rate of excitation may be uniform or time-dependent: In either case, we may write that the probability of excitation in the interval dt_0 is $\sigma(t_0)dt_0$.

The effect of a perturbation on a rate process is determined by its effect on the initial state. If, therefore, the state from which the atoms are excited is not perturbed by the electric field (which will be true for the $1^2S_{1/2}$ state in hydrogen), the rate at which atoms are introduced into state $|b\rangle$ will be independent of V.

5. STEADY-STATE SITUATION

Before we take up the question of modulated excitation, it is worth while verifying that the analysis of Secs. 2 and 3 yields a sensible result for the case of excitation at a uniform rate. Using Eq. (8) with $(t-t_0)$ for t, and setting $\sigma(t_0) = r$, a constant, we find that the intensity of radiation at time t from an assembly of

atoms excited to state $|b\rangle$ at a uniform rate is

$$I(t)=r\int_0^t I(t,t_0)dt_0$$

$$=K\left\{\frac{c_1}{\gamma/2-p}+\frac{c_2}{(\gamma/2+p)}+\frac{(\alpha\gamma-2\beta q)}{(\gamma^2/4+q^2)}\right\}, \quad (10)$$

where K is a constant. The steady-state intensity is independent of time, as one would require.

With the help of Eqs. (6) and (9), the sum of the three terms in square brackets may be reduced to $1/\gamma$. This result is the analytical justification of the remark that the intensity of the fluorescent light is independent of ω and $|V|$, that is, independent of the degree of mixing of states $|a\rangle$ and $|b\rangle$. To interpret this result, it is not sufficient to think merely in terms of populations and decay rates. It is tempting to argue that the modified decay constants of state $|b\rangle$ just compensate the fact that some of the excited atoms are transferred by the perturbation to the nonradiating state $|a\rangle$. This is to overlook the cross term (the third term) in Eq. (10), which expresses the correlation between the partial probability amplitudes B_1 and B_2. The contribution of the cross term is not negligible: Its value, to first order in $|V|^2$, is $-|V|^2\gamma/(\gamma^2/4+\omega^2+4|V|^2)^2$. Nevertheless, the conclusion is entirely acceptable that if atoms are excited to the state $|b\rangle$ at a uniform rate, then the intensity of the fluorescent light from state $|b\rangle$ should be independent of the perturbation.

6. MODULATED EXCITATION

Suppose that the rate of excitation is modulated at the angular frequency f. We write $\sigma(t_0)=r(1+\cos ft_0)$, and proceed as in the last section.
We have

$$I(t)=r\int_0^t (1+\cos ft_0)I(t,t_0)dt_0$$

$$=K\{A+B\cos ft+C\sin ft\}, \quad (11)$$

where

$$A=\frac{c_1}{\gamma/2-p}+\frac{c_2}{\gamma/2+p}+\frac{(\alpha\gamma-2\beta q)}{\gamma^2/4+q^2}=\frac{1}{\gamma},$$

$$B=\frac{c_1(\gamma/2-p)}{(\gamma/2-p)^2+f^2}+\frac{c_2(\gamma/2+p)}{(\gamma/2+p)^2+f^2}$$
$$+\frac{\frac{1}{2}[\alpha\gamma-2\beta(q+f)]}{\gamma^2/4+(q+f)^2}+\frac{\frac{1}{2}[\alpha\gamma-2\beta(q-f)]}{\gamma^2/4+(q-f)^2},$$

and

$$C=\frac{c_1 f}{(\gamma/2-p)^2+f^2}+\frac{c_2 f}{(\gamma/2+p)^2+f^2}$$
$$+\frac{\frac{1}{2}[2\alpha(q+f)+\beta\gamma]}{\gamma^2/4+(q+f)^2}-\frac{\frac{1}{2}[2\alpha(q-f)+\beta\gamma]}{\gamma^2/4+(q-f)^2}.$$

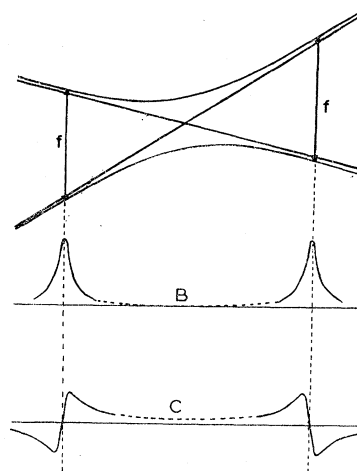It is predicted that the fluorescent light should be modulated, and that the amplitude and phase of the

FIG. 3. Resonance effects in the amplitude of the cosine component of the modulation (B) and the sine component (C) when $f\gg\gamma$.

modulation should depend on ω, γ, $|V|$, and f. We shall consider the variations with ω, regarding the other quantities as parameters. It is convenient to consider the functions B and C separately. Experimentally, they can be isolated by phase-sensitive detection of the modulated component of a photoelectric signal.

The variations of B and C are of two types. The cross terms (those containing α and β) exhibit resonance phenomena when $\pm q$ (the separation of the perturbed levels) is in the neighborhood of f. These we shall study under the condition ω (and therefore q, and therefore f) $\gg\gamma/2$. On the other hand, when $f\ll\gamma/2$, the direct terms in B and C which have the coefficient c_1 are sensitive to the relative magnitudes of f and $|V|$. This will yield changes in the magnitudes of B and C in the region of the level crossing. We shall study this effect under the condition $|V|\ll\gamma/2$, which simplifies the analysis and leads to the greatest precision in the location of the level crossing, though it is not a necessary restriction.

A. Resonance Effects

By choosing f sufficiently large, the resonance terms in B and C, those with the denominators $\{\gamma^2/4+(q\pm f)^2\}$, dominate the others. These terms are combinations of slightly distorted Lorentzian and dispersion-type functions, both of which go through resonance when $\pm q=f$. Sufficiently far away from the region of the intersection the value of q will be only slightly different from ω, the unperturbed separation of the levels. Although we are regarding ω as the primary variable, it is analytically simpler to regard the resonances as functions of q.

The distortion is due to the slow variation of α and β with ω. The width at half intensity of the Lorentzian component (as a function of q) is γ, so that the condition for separation of the resonance terms from the background is $f\gg\gamma$. The relative contributions of the Lorentzian and dispersion components in the region of

resonance is α/β in the case of B and β/α in the case of C. In the approximations $|V|^2 \ll (\gamma^2/4+\omega^2+4|V|^2)$, $\omega \gg \gamma/2$, we find $\alpha/\beta \rightarrow \omega/\gamma$. These approximations are valid sufficiently far away from the region of intersection, so that the Lorentzian component will be dominant in the cosine component of the modulation (B) and the dispersion shape in the sine component (C). (See Fig. 3.)

B. Level-Crossing Effects

As f is reduced below γ, the resonance curves on either side of the intersection draw together, while the background terms assume a relatively greater importance. The sum of the terms C is smaller than the sum B in the ratio $f/(\gamma/2)$, that is to say, the phase of the modulation remains almost constant as the intersection is traversed. We shall consider the variation of the only significant contribution to the amplitude B.

Under the approximations $|V| \ll \gamma/2$, $f \ll \gamma/2$, the last three terms in B sum to $(1-x^2)/\gamma$, where $x^2 = |V|^2/(\gamma^2/4+\omega^2)$. The first term, $c_1(\gamma/2-p)/\{(\gamma/2-p)^2+f^2\}$, reduces to 0 if $(f/\gamma) \gg x^2$ and x^2/γ if $(f/\gamma) \ll x^2$. Hence, as $f \rightarrow 0$, the amplitude of modulation of the fluorescent light becomes independent of ω and $|V|$, which is in satisfactory agreement with the result obtained for the limiting case when the rate of excitation is constant. On the other hand, if $f \gg |V|^2\gamma/(\gamma^2/4+\omega^2)$, one will expect to find changes in the amplitude of modulation given by

$$B = \{1 - |V|^2/(\gamma^2/4+\omega^2)\}/\gamma, \qquad (12)$$

namely, a resonance curve of width γ at half-intensity, centered on $\omega=0$. It will be noticed that if the condition $f \gg |V|^2\gamma/(\gamma^2/4+\omega^2)$ is satisfied at $\omega=0$, it will be satisfied also for nonzero values of ω.

7. DISCUSSION

The resonance effects predicted in Sec. 6.A bear an interesting relation to the conventional type of double resonance experiment. In such experiments an *oscillating* electric field is used to induce transitions from $|b\rangle$ to $|a\rangle$ in an assembly of atoms excited at a uniform rate. The peak of the resonance curve is found when the applied frequency is equal to ω, the interval between the unperturbed levels. In the present case a *static* electric field induces transitions for which the frequency of resonance is zero. The frequency q is that at which the probability amplitudes oscillate between

$|b\rangle$ and $|a\rangle$. The phase of this nutational motion is not synchronous for different atoms when the rate of excitation is uniform, but it becomes so if the process of excitation is modulated at the nutational frequency. One finds a resonance in the amplitude of modulation of the fluorescent light at the frequency q, not ω. The difference between q and ω is small and could be estimated in any particular case, but it might be possible to find the position of the crossing point without applying this correction by studying the resonances on either side of the intersection, since the displacements of the two peaks are equal and in opposite directions.

The level-crossing experiment suggested in Sec. 6.B should yield a symmetrical curve whose peak corresponds to the point of intersection of the unperturbed levels. The fields and frequencies for studying such curves in the $n=2$ states of hydrogen are easily within reach. Crossing points for which $\Delta m = \pm 1$ (in the notation of Lamb,[6] these are βe, αc and βd) are found at approximately 500, 4500, and 7000 G, respectively. For the first of these the perturbation $|V|$ introduced by thermal motion at right angles to the field H allows the conditions under which Eq. (12) was derived to be satisfied. The conditions were $4|V|^2/\gamma^2 \ll f/\gamma \ll \frac{1}{2}$. The value of $\gamma/2\pi$ for the states $2^2P_{1/2}$ is close to 100 Mc/sec. Taking $v=2.4\times10^5$ cm/sec, the mean thermal velocity at $0°C$, $E=(v/c)\times H$ is approximately 1.3 V/cm and $|V|/2\pi$ approximately 2.4 Mc/sec. The choice $f/2\pi=3$ Mc/sec then yields $f/\gamma=3\times10^{-2}$, which lies conveniently between $\frac{1}{2}$ and $4|V|^2/\gamma^2=2.3\times10^{-3}$.

The larger fields at the crossing points αc and βd increase the electric field due to thermal motion to the point where the approximations are not justified, but if f is increased to be at least comparable with $4|V|^2/\gamma$, the predicted effects should still be observable. The approximation $|V| \ll \gamma/2$ was introduced merely to simplify the analysis. As f is increased the resonance curves will widen, but should still remain symmetrical.

The crossing βf, which occurs at about 1000 G requires a component of E parallel to H which the motional electric field cannot provide. For this crossing, an applied electric field of a few volts per cm would be necessary.

[6] W. E. Lamb and R. C. Retherford, Phys. Rev. **79**, 549 (1950).