

Radiation Damping and the Polarization of Fluorescence Radiation

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If the distance between two or more energy levels is comparable to their natural breadth, the levels cease to act independently. The coupling between the levels is then describable by means of a "damping constant matrix." The usual discussions concern themselves with a diagonal damping constant. Below a systematic treatment of emission, absorption and fluorescence is given without this restriction and it is shown how in general the frequencies

of emission lines are affected by this radiation coupling. The theory is applied to the calculation of the polarization of fluorescence radiation. It is shown that the coupling state of the lower group of levels of the fluorescence line does not influence the polarization. Results of detailed calculations are given for the polarization of $H\alpha$ excited by absorption of the second line of the Lyman series.

PHENOMENA associated with radiation damping have been treated by various authors¹⁻⁵ from the point of view of Dirac's theory of light quanta. In most of the phenomena investigated the effect of the coupling of matter and radiation turned out to be that of broadening the sharp line emission of frequency $\nu = \Delta W/h$ into a band of width proportional to the damping constant. It has been shown by Weisskopf and Wigner² that the width of the frequency band may be thought of as the sum of the widths of the initial and final level. In this way the old question of diffuse quantization has found its quantitative treatment. One may say that on account of the coupling between radiation and matter the concept of the stationary state is only partially exact and that the finite life of the stationary states makes their energy diffuse to the degree demanded by the uncertainty relation. The question arises whether the effect of the interaction with radiation is entirely that of broadening the energy levels or may also produce more vital effects on the quantization. In order to discuss this one must give a definition of quantization which applies in the presence of a damping constant. If the frequency spectrum emitted by an atom is of the type $const. \times [(\nu - \nu_0)^2 + \Gamma^2]^{-1}$ we may say that the energy difference between the initial and final level is $h\nu_0$ and that the sum of the widths of the levels corresponds to a damping constant Γ . We can thus measure ν_0 even though the energy is diffuse just as we can

measure the center of gravity of a wave packet in a properly defined state even though the position of the particle is indefinite. Let there be two levels close together situated so that the combination frequencies to a third level, as calculated by neglecting the coupling to radiation and given by the Bohr frequency condition, are ν_1, ν_2 . In some cases it is possible to prepare an atomic state of such a kind that one will have a frequency distribution $[(\nu - \nu_1)^2 + \Gamma_1^2]^{-1} d\nu$ emitted, and to prepare another state the emission from which will be $[(\nu - \nu_2)^2 + \Gamma_2^2]^{-1} d\nu$. In such cases we may say that the coupling to the radiation had only a broadening effect. We are particularly concerned with another condition which makes it impossible to prepare such states. The general case⁶ is one in which the spectra that may be prepared are of the form $[(\nu - f_1(\nu_1, \nu_2))^2 + \Gamma_1^2]^{-1}$ and $[(\nu - f_2(\nu_1, \nu_2))^2 + \Gamma_2^2]^{-1}$. In this condition the effect of the coupling to the radiation is not only to broaden each line, but also to shift its center of gravity. We shall first discuss qualitatively these effects for emission, absorption and fluorescence.

(a) *Emission.* A complete treatment of the emission of radiation from nondegenerate states has been given by Weisskopf and Wigner. It applies only as long as the energy levels of the atomic system are separated by intervals which are appreciably larger than the natural breadth due to radiation damping. When this is not the case one has to work⁶ with a "damping constant matrix" instead of an ordinary "damping constant." Thus consider two energy levels μ, μ' located so close to each other that their energy

¹ F. Hoyt, *Phys. Rev.* **36**, 860 (1930).

² V. Weisskopf and E. Wigner, *Zeits. f. Physik* **63**, 54 (1930).

³ V. Weisskopf, *Ann. d. Physik* **9**, 23 (1931).

⁴ E. Fermi, *Rev. Mod. Phys.* **4**, 87 (1932).

⁵ G. Breit, *Rev. Mod. Phys.* **5**, 91 (1933).

⁶ Reference 5. See Eq. (156), p. 118. The special case of the text above corresponds to $\Gamma^{\mu\mu'}$ being diagonal.

difference is comparable with their average natural breadth. If the atom is put into the level μ , its coupling to the radiation will produce intermediate states of nearly the same energy in which a light quantum has been emitted and these intermediate states, through the absorption of a light quantum, will cause the production of μ' . Only in special cases will the radiation be describable as a simple exponential decay of the probability of the level μ , as may be seen without elaborate calculation by means of the following argument. Suppose for the moment that μ and μ' are two states such that either can emit independently of the other and suppose that they result from the application of an external, say magnetic, field to a degenerate level. Let their wave functions be ψ_μ and $\psi_{\mu'}$. We may as a rule neglect the change in ψ_μ and $\psi_{\mu'}$ due to the field. For the important thing about these wave functions is their effect on matrix elements to other levels and if these elements are appreciable before the field is applied, we may neglect the small change produced in them by the field. Let now the magnetic field be removed and a field of another type, say an electric field, be applied. The new energy levels will be described by $\psi_{\bar{\mu}} = c_1\psi_\mu + c_2\psi_{\mu'}$, $\psi_{\bar{\mu}'} = c_3\psi_\mu + c_4\psi_{\mu'}$. Neither $\psi_{\bar{\mu}}$ nor $\psi_{\bar{\mu}'}$ can now decay exponentially since the rate of decay is, in general, different for μ and μ' . This discussion applies only to very weak fields since energy differences also enter the exponents.⁷

A brief treatment of this question has been given by Bethe⁸ for the case of hydrogen. He showed how the metastability of the $2s$ level is removed by a weak electric field and how, as the field decreases to zero, one approaches continuously to the existence of a metastable level. Bethe's treatment makes no explicit use of the theory of light quanta. It is not altogether rigorous because the form of the result is assumed without proof. One may regard some of the calculations which follow as substantiating the validity of this form.

The radiation coupling discussed here is

similar, but not identical with, that treated by Weisskopf and Wigner² for a harmonic oscillator. In both cases it is essential that the radiation emitted in a jump between two energy levels be of the right frequency to be selectively absorbed in a transition between another pair. In our calculations the lower levels of the two pairs are either identical or close together and the energy differences of the two pairs are not equal. In these respects the coupling considered here is different from that of Weisskopf and Wigner. In neither case is the coupling describable as the result of the addition of probabilities for emissions and absorptions. It is correctly thought of only in terms of additions of probability amplitudes.

(b) *Absorption and fluorescence radiation.* A treatment of absorption and of the polarization of resonance radiation has been given by Weisskopf.³ His results apply either to nondegenerate systems or to the special case of a nondegenerate normal level and a triply degenerate excited level with constant angular momentum. A more complete theory given by Breit⁵ took into account explicitly possible degeneracies (hyperfine structure) of both levels for resonance radiation, and applied the results to cases of constant angular momentum as well as some closely related cases in which the "damping constant matrix" is diagonal. In weak magnetic fields only the splittings of the upper group of levels and their mean life were found to be of importance. It will be seen below⁹ that as long as the incident radiation has a uniform energy spectrum¹⁰ this result applies also to fluorescence radiation. The natural breadths and the energy differences among the lower group of levels do not matter for the polarization of this radiation. On the other hand, according to Weisskopf and Wigner,² it is the sum of the breadths of the initial and final levels that determines the width of the emission lines. It is thus impossible to replace the fluorescence transition by a virtual oscillator, since

⁷ The fact that the damping constants of atoms with a constant angular momentum are necessarily equal, by spectroscopic stability, is not an objection to the above argument because the angular momentum need not be constant.

⁸ H. Bethe, *Handb. d. Physik*, H. Geiger and K. Scheel; Springer, 1933, 2nd edition XXIV/1, pp. 452-456.

⁹ I. S. Lowen and G. Breit, *Phys. Rev.* **45**, 120 (1934).

¹⁰ If the incident energy spectrum is non-uniform the splitting of the normal level affects the result, as is obvious from qualitative considerations and also appears in Eq. (7.4) below. The splitting and width of the lower level c of the energy level pair giving the fluorescence line is immaterial also in this case as follows by combining Eq. (7.4) with Eq. (7.8).

the damping constant of that oscillator varies for different phenomena.

The same is found to be true if the damping constant is nondiagonal. The lack of influence of the lower level may be understood qualitatively in the sense that the cause of broadening is unimportant within certain limits. Thus if this level is split by interaction with the nuclear spin there is no effect on the polarization,⁵ just as there is no effect if it is broadened by possible transitions to levels below it.

(c) *Fluorescence of hydrogen.* For purposes of illustration of the general theory we calculate the polarization of the line $H\alpha$ produced by absorption of the second line of the Lyman series. The atomic hydrogen gas is supposed to be in an electric field. The polarization changes as the electric field increases as soon as the Stark effect splittings are of the order of the natural breadth of the $n=3$ sublevels. No explicit calculations were made for the influence of the nuclear spin which must affect the polarization in weak fields. If the experimental arrangement for observing the polarization of such fluorescence should prove practical, we should be able to determine the h.f.s. of the $3s$ level of hydrogen by measurements of the polarization of the fluorescent $H\alpha$ radiation.

1. GENERAL THEORY

An absorbing atom in the normal state a is supposed to be exposed to radiation from a distant emitting atom I. The state a as well as the other states with which we deal is supposed to consist of groups of sublevels such as would be produced by applying an external field to a degenerate level. The maximum frequency difference between sublevels in the same group is supposed to be small in comparison with the emission and the absorption frequencies dealt with. The same is supposed to hold for the damping constants. No restriction on the relative magnitudes of damping constants and the frequency differences of sublevels in the same group is made. The frequency ν_I of the incident radiation is supposed to lie close to the absorption frequency from a to another state b . We also take into account the presence of two other states c, d (Fig. 1) to which the atom may fall in succession from b . The light quanta emitted are called s, s' , respectively. The state d is supposed to be metastable. The above arrangement of levels enables one to generalize to most of the other possible cases. The equations which describe the process are¹¹

$$[(d/idt) + \omega(b')]C(b') = \sum(sc')(B_s^{c'b'})^*C(sc') + \sum(sa')(B_s^{a'b'})^*C(sa') \\ + K_{b'a} \exp \{ -i[\omega(I) + \omega(a) - i\gamma(I)]t \} \dots, \quad (1.1)$$

$$[(d/idt) + \omega(c') + \omega(s)]C(sc') = \sum(b')B_s^{c'b'}C(b') + \sum(d's')(B_s^{d'c'})^*C(ss'd') \dots, \quad (1.2)$$

$$[(d/idt) + \omega(d') + \omega(s) + \omega(s')]C(ss'd') = \sum(c')B_s^{d'c'}C(sc'). \quad (1.3)$$

Here C are the probability amplitudes for the states considered. Thus, e.g., $C(ss'd')$ refers to the state in which there is one light quantum of type s , one light quantum of type s' , and in which the atom is in a sublevel d' of the state d . We use a and a' , b and b' , etc. interchangeably for the sublevels of a, b , etc. The additive energy constant is supposed to be adjusted so that the energy is zero if there are no light quanta and if the atom is in an arbitrarily chosen sublevel of a . Also $\omega = 2\pi\nu$

$$B_s^{ab} = (\hbar\nu_s V)^{-\frac{1}{2}} (\sum e_i \dot{\mathbf{r}}_i \mathbf{f}_s)_{ab} \exp \{ -i\mathbf{k}_s \mathbf{R} \} \quad (1.4)$$

where

\mathbf{f}_s = unit vector in the direction of electric intensity of light quantum s .
 e_i and $\dot{\mathbf{r}}_i$ = charge and velocity vector of atomic particle i .
 \mathbf{k}_s = vector of magnitude $2\pi c/\nu_s$ in the direction of propagation of light quantum s .
 \mathbf{R} = vector from origin of coordinates to center of atom and

$$K_{ba} = (\sum e_i \dot{\mathbf{r}}_i)^{(p)}_{ba} (e \dot{\mathbf{r}}_I)^{(p)}_{n_I n_I'} / R_{II} \hbar c^2 \quad (1.5)$$

where the superscript (p) changes a vector into its projection on the plane perpendicular to the line joining the emitter I to the absorber, and where n_I, n_I' are, respectively, the normal and excited states of the emitter.

We solve these equations using the customary approximations introduced by Dirac, Weisskopf

¹¹ Reference 5, VII §4; VI §4.

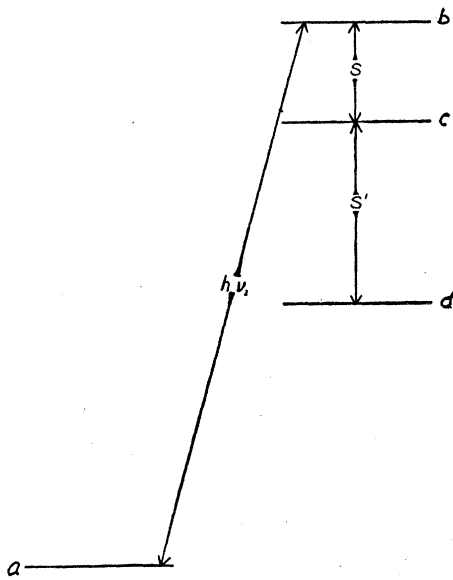


FIG. 1. Energy diagram.

and Wigner and by Hoyt. Thus the summations over possible light quanta on the right side of Eq. (1) will be replaced by integrations. These will be performed approximately by extending the range to $-\infty$ and by considering the number of possible kinds of light quanta in unit frequency range as being constant. The procedure for obtaining the solutions is very similar to that of the simpler case already discussed.¹¹ We introduce the following abbreviations:

$$\begin{bmatrix} A \\ B \end{bmatrix} = e^{-iAt} - e^{-iBt};$$

$$\left[\begin{bmatrix} A \\ B \end{bmatrix} \right] = \left[\begin{bmatrix} A \\ B \end{bmatrix} \right] / (B - A) \quad (2)$$

and we have

$$\int_{-\infty}^{+\infty} \left[\begin{bmatrix} A \\ B \end{bmatrix} \right] dB = \pi i e^{-iAt}. \quad (3)$$

The description of the emission from c to d is obtained by solving Eqs. (1.2), (1.3) omitting the first sum in Eq. (1.2) altogether. The solution is

$$C(sc') = \sum (Ka^{-1})_{s\bar{c}} a_{c'\bar{c}} \left[\begin{bmatrix} \Omega - i\Gamma \\ \omega(\bar{c}) + \omega(s) - i\gamma(\bar{c}) \end{bmatrix} \right], \quad (5.1)$$

$$C(ss'd') = \sum (Ka^{-1})_{s\bar{c}} a_{c'\bar{c}} B_{s',d'c'} \left[\begin{bmatrix} \Omega - i\Gamma \\ \omega(d') + \omega(s) + \omega(s') \end{bmatrix} \right] - \left[\begin{bmatrix} \omega(\bar{c}) + \omega(s) - i\gamma(\bar{c}) \\ \omega(d') + \omega(s) + \omega(s') \end{bmatrix} \right] / [\omega(s) + \omega(\bar{c}) - i\gamma(\bar{c}) - \Omega + i\Gamma], \quad (5.2)$$

$$C(sc') = \sum (\bar{c}) a_{\bar{c}} a_{c'\bar{c}} \exp \{ -i[\omega(\bar{c}) + \omega(s) - i\gamma(\bar{c})] \}, \quad (4.1)$$

$$C(ss'd') = \sum a_{\bar{c}} a_{c'\bar{c}} B_{s',d'c'} \left[\begin{bmatrix} \omega(\bar{c}) + \omega(s) - i\gamma(\bar{c}) \\ \omega(d') + \omega(s) + \omega(s') \end{bmatrix} \right], \quad (4.2)$$

where the $a_{\bar{c}}$ are determined by

$$\sum a_{\bar{c}} a_{c'\bar{c}} = C(sc')_{t=0} \quad (4.3)$$

and $a_{c'\bar{c}}, \omega(\bar{c}), \gamma(\bar{c})$ are given by

$$a_{c'\bar{c}} [\omega(c') - \omega(\bar{c}) + i\gamma(\bar{c})] = i \sum \gamma^{c'c''} a_{c''\bar{c}} \quad (4.4)$$

with

$$\gamma^{c'c''} = (\pi / \Delta\omega(s')) \overline{\sum (d') (B_{s',d'c'})^* B_{s',d'c''}}, \quad (4.5)$$

where the $\overline{\quad}$ indicates averaging over all directions and polarizations of s' .

Eq. (5.3) gives, in general, nonvanishing values of all $a_{\bar{c}}$. It is thus not possible to have only one level c' of the group c excited at all times. If it is the only excited level at $t=0$ other levels will become excited later according to Eq. (4.1). If the levels $c', c'',$ etc., are widely spaced, the solutions of the Eqs. (4.4) will be such that a possible \bar{c} will lie close to a c' and the $a_{c'\bar{c}}$ for this pair of values will be much larger than the other $a_{c'\bar{c}}$; the emission can then take place with the excitation of only one level c' . If, however, the differences $\omega(c') - \omega(c'')$ are of the same order as the $\gamma^{c'c''}$ then one should take into account more than one term in Eq. (4.1) and the energy levels lose their identity as the radiation couples them by the matrix $\gamma^{c'c''}$. The quantity $\omega(s)$ is, of course, irrelevant to the discussion of emission, playing the part of an additive constant in the energy.

In the solution of Eqs. (1) the terms in $C(b')$ will bring into Eq. (1.2) terms of the type $K_{s,c'} \exp \{ -i(\Omega - i\Gamma)t \}$. We consider this equation with one of these terms replacing the first sum. We obtain the following solution of the thus modified Eqs. (1.3), (1.2) subject to the initial conditions $C(sc') = C(ss'd') = 0$

the summations being over \bar{c} and where $(Ka^{-1})_{s\bar{c}}$ is defined by:

$$\sum (Ka^{-1})_{s\bar{c}} a_{c'\bar{c}} = K_{sc'}. \quad (5.3)$$

This solution except for the presence of $\omega(s)$ is of the same form as the absorption solution from d to c , and its properties have been already partly discussed.¹¹ Using Eqs. (5.1), (5.2), (3) we solve Eqs. (1.1), (1.2), (1.3) subject to the initial conditions $C(b') = C(sc') = C(ss'd') = 0$ and obtain

$$C(b') = \sum (\bar{b})(KA^{-1})_{\bar{b}a} A_{b'\bar{b}} \left[\begin{array}{c} x \\ z \end{array} \right], \quad (6.1)$$

$$C(sc') = \sum (\bar{b}\bar{c})(KA^{-1})_{\bar{b}a} A_{b'\bar{b}} B_{s'c''b'} (a^{-1})_{\bar{c}c''} a_{c'\bar{c}} \left[\left[\begin{array}{c} x \\ u \end{array} \right] - \left[\begin{array}{c} z \\ u \end{array} \right] \right] / (z-x), \quad (6.2)$$

$$C(ss'd') = \sum (KA^{-1})_{\bar{b}a} A_{b'\bar{b}} B_{s'c''b'} (a^{-1})_{\bar{c}c''} a_{c'\bar{c}} B_{s'd'e'} (z-x)^{-1} \\ \times \left[\left(\left[\begin{array}{c} x \\ y \end{array} \right] - \left[\begin{array}{c} u \\ y \end{array} \right] \right) (u-x)^{-1} - \left(\left[\begin{array}{c} z \\ y \end{array} \right] - \left[\begin{array}{c} u \\ y \end{array} \right] \right) (u-z)^{-1} \right], \quad (6.3)$$

where

$$A_{b'\bar{b}} [\omega(b') - \omega(\bar{b}) + i\gamma(\bar{b})] = i \sum \gamma^{b'b''} A_{b''\bar{b}}, \quad (6.4)$$

$$x = \omega(I) + \omega(a) - i\gamma(I), \quad y = \omega(d') + \omega(s) + \omega(s'), \quad z = \omega(\bar{b}) - i\gamma(\bar{b}), \quad u = \omega(\bar{c}) + \omega(s) - i\gamma(\bar{c}). \quad (6.5)$$

On account of the presence of $\gamma(\bar{b})$ in z and $\gamma(\bar{c})$ in u both $C(b')$ and $C(sc')$ vanish when $t \rightarrow \infty$. The only terms in $C(ss'd')$ which do not vanish are those due to y in the $\left[\begin{array}{c} \cdot \\ y \end{array} \right]$. Thus for sufficiently large t

$$C(ss'd') = \sum (\bar{b}\bar{c})(KA^{-1})_{\bar{b}a} (ABa^{-1})_{s\bar{c}} (aB)_{s'd'} [X - \omega(s) - \omega(s')]^{-1} [Z(\bar{b}) - \omega(s) - \omega(s')]^{-1} \\ \times [U(\bar{c}) - \omega(s')]^{-1} \exp \{ -i[\omega(d') + \omega(s) + \omega(s')]t \}, \quad (7.1)$$

where

$$X = \omega(I) - \omega(d') - i\gamma(I); \quad Z(\bar{b}) = \omega(\bar{b}d') - i\gamma(\bar{b}); \quad U(\bar{c}) = \omega(\bar{c}d') - i\gamma(\bar{c}). \quad (7.2)$$

The above expression (7.1) gives the final values for the probability amplitudes of states in which, light quanta s, s' were emitted, respectively, in transitions $b \rightarrow c, c \rightarrow d$ and the atom fell into state d' . In order to obtain the probability of finding simultaneously a photon s with a given polarization and directional property and a photon s' with another polarization and directional property we must calculate

$$\sum_{\omega(s)\omega(s')} |C(ss'd')|^2 = [1/\Delta\omega(s)\Delta\omega(s')] \int_0^\infty \int_0^\infty |C(ss'd')|^2 d\omega(s) d\omega(s'), \quad (7.3)$$

where $1/\Delta\omega(s)$ is the number of photons of the type considered in the unit frequency range of $\omega(s)$. Using Eqs. (7.1), (7.2), we have

$$\sum_{\omega(s)\omega(s')d'} |C(ss'd')|^2 = \frac{2\pi^2}{i\gamma(I)\Delta\omega(s)\Delta\omega(s')} \frac{\sum (\bar{b}'\bar{c}'\bar{b}\bar{c})}{[\omega(\bar{c}\bar{c}') - i(\gamma(\bar{c}') + \gamma(\bar{c}))][\omega(\bar{b}\bar{b}') - i(\gamma(\bar{b}') + \gamma(\bar{b}))]} \\ \left\{ \frac{1}{\omega(\bar{b}'a) - \omega(I) + i(\gamma(\bar{b}') + \gamma(I))} + \frac{1}{\omega(I) - \omega(\bar{b}a) + i(\gamma(I) + \gamma(\bar{b}))} \right\}, \quad (7.4)$$

$$(\bar{b}'\bar{c}' | G | \bar{b}\bar{c}) = \sum (KA^{-1})_{\bar{b}'a} (ABs_a^{-1})_{\bar{c}'\bar{b}'} (aB_{s'})_{\bar{c}d'} (aB_{s'})_{\bar{c}d'} (ABs_a^{-1})_{\bar{c}\bar{b}} (KA^{-1})_{\bar{b}a}. \quad (7.5)$$

For large $\gamma(I)$ the general Eq. (7.4) simplifies to

$$\sum |C(ss'd')|^2 = \frac{4\pi^2}{\gamma^2(I)\Delta\omega(s)\Delta\omega(s')} \frac{\sum (\bar{b}'\bar{c}'\bar{b}\bar{c})}{[\gamma(\bar{c}') + \gamma(\bar{c}) + i\omega(\bar{c}\bar{c}')][\gamma(\bar{b}') + \gamma(\bar{b}) + i\omega(\bar{b}\bar{b}')]} (\bar{b}'\bar{c}' | G | \bar{b}\bar{c}). \quad (7.6)$$

From this Eq. (7.6) one can obtain the properties of the radiation s emitted in jumps from b to c or the properties of the radiation s' emitted in jumps from c to d by summing, respectively, over all the directions of polarization and of propagation of s' and s , respectively. We make the calculation for s and we must thus average $(\bar{b}'c'|G|\bar{b}\bar{c})$ over all possible polarizations of s' . We have by Eq. (4.5)

$$(\pi/\Delta\omega(s'))\sum\overline{(d')(aB_{s'})\bar{c}'a'^*(aB_{s'})\bar{c}a'} = \sum(c'c'')a_{c''}\bar{c}'^* \gamma^{c''c'} a_{c'}\bar{c}. \quad (7.7)$$

But it follows from Eq. (4.4) that

$$\sum(c'c'')a_{c''}\bar{c}'^* \gamma^{c''c'} a_{c'}\bar{c} = (1/2)[\gamma(\bar{c}) + \gamma(\bar{c}') + i\omega(\bar{c}\bar{c}')] \sum(c)a_{c'}\bar{c}'^* a_{c'}\bar{c}. \quad (7.8)$$

Hence

$$\sum|\overline{C(ss'd')}|^2 = (2\pi/\gamma^2(I)\Delta\omega(s))\sum(\bar{b}\bar{b}')\beta(\bar{b}'\bar{b})\kappa(\bar{b}\bar{b}')/[\gamma(\bar{b}) + \gamma(\bar{b}') + i\omega(\bar{b}\bar{b}')], \quad (9)$$

where

$$\beta(\bar{b}'\bar{b}) = \sum(c)(AB_s)\bar{c}\bar{b}'^*(AB_s)\bar{c}\bar{b} \dots \quad (9.1) \quad \kappa(\bar{b}\bar{b}') = \sum(a)(KA^{-1})_{b'a}^*(KA^{-1})_{\bar{b}a}. \quad (9.2)$$

It is seen from Eq. (9) that the frequency differences among levels c do not matter for the intensity of fluorescence radiation due to light quanta s . Neither do the damping constants $\gamma^{c''c'}$ enter the result. Thus the breadth of the lower level has nothing to do with the polarization of the fluorescence radiation.

In the above calculation we considered explicitly only the level groups a, b, c, d . The presence of other level groups introduces no essential difference. Thus the matrix $\gamma^{b'b''}$ is given by a formula similar to (4.5):

$$\gamma^{b'b''} = (32\pi^4 e^2/3hc^3)[\sum(d)\nu^3(bd)\mathbf{r}(b'd)\mathbf{r}(db'') + \sum(c)\nu^3(bc)\mathbf{r}(b'c)\mathbf{r}(cb'') + \sum(a)\nu^3(ba)\mathbf{r}(b'a)\mathbf{r}(ab'')].$$

Similarly there is, in general, a like term for every group of levels below b to which a transition is possible.

Eq. (7.1) is more general than the formula derived by Weisskopf¹² inasmuch as it includes non-diagonal damping terms. It is more special inasmuch as it does not consider chains of more than two successive reemissions and because it does not include the different permutations in the order of emission of the light quanta. An obvious extension of Eq. (7.1) can be made by including in it the extra terms of Weisskopf's formula.

2. APPLICATION TO HYDROGEN IN AN ELECTRIC FIELD

We consider an atom of hydrogen in an electric field. We suppose the field to be weak enough to have the Stark effect small in comparison with the distances between levels with different j . We may then approximate the wave function¹³ by considering it as a linear combination of wave functions with the same j, m and different l . We calculate the contribution to $\gamma^{b'b''}$ due to a level of total quantum number n' . In terms of $(32\pi^4\nu(nn')^3e^2/3hc^3)$ this contribution is

$$\frac{2j+3}{8(j+1)}(R_{n', j+3/2}^{n, j+1/2})^2 + \frac{2j+1}{8(j+1)}(R_{n', j-1/2}^{n, j+1/2})^2 + (-)^{\alpha'+\alpha''} \left[\frac{2j+1}{8j}(R_{n', j+1/2}^{n, j-1/2})^2 + \frac{2j-1}{8j}(R_{n', j-3/2}^{n, j-1/2})^2 \right]. \quad (10)$$

Here n is the total quantum number of the state $b, R_{n', l}^{n, l}$ is the radial integral of r , referred to the states n, l and n', l' ; for $\alpha'=0, 1$ the state b' is, respectively, symmetric and antisymmetric, its wave function being supposed to be:¹⁴

$$2^{-3}\{(n, j+\frac{1}{2}, j, m) + (-)^{\alpha}(n, j-\frac{1}{2}, j, m)\}.$$

¹² V. Weisskopf, Zeits. f. Physik **85**, 451 (1933).

¹³ R. Schlapp, Proc. Roy. Soc. **A119**, 313 (1928); V. Rojansky, Phys. Rev. **33**, 1 (1929).

¹⁴ Since the result depends only on $\alpha+\alpha'$ and not on

α, α' individually, the choice of signs for the wave functions (n, l, j, m) is immaterial for the present purpose. The radial and angular parts of the wave functions are supposed to be normalized to 1 separately.

Expression (10) has values for the states of interest to us given in Table I.

TABLE I.

n	n'	j	$(3hc^3/32\pi^4\nu(nn')^3e^2)\gamma^{b'b''}$
3	2	3/2	$(1/5)(R_{2p}^{3d})^2 + (-)^{\alpha+\alpha'}(1/6)(R_{2s}^{3p})^2$
3	1	3/2	$(-)^{\alpha+\alpha'}(1/6)(R_{1s}^{3p})^2$
3	2	1/2	$(1/6)(R_{2s}^{3p})^2 + (-)^{\alpha+\alpha'}(1/2)(R_{2p}^{3s})^2$
3	1	1/2	$(1/6)(R_{1s}^{3p})^2$

The second and fourth lines give also the values for $n=2$, $n'=1$ on changing $3p$ into $2p$ and $3s$ into $2s$. The Eqs. (4.4) are now

$$(\bar{\Gamma} - \Gamma_1)A_1 = gA_2; \quad (\bar{\Gamma} - \Gamma_2)A_2 = gA_1, \quad (11)$$

where

$$\bar{\Gamma} = \bar{\gamma} + i\bar{\omega}, \quad \Gamma_1 = \gamma + i\omega_1, \quad \Gamma_2 = \gamma + i\omega_2, \quad \gamma^{12} = g, \quad \gamma^{11} = \gamma^{22} = \gamma \quad (11.1)$$

and by 1,2 are meant, respectively, the symmetric and antisymmetric states. There are two roots for Γ which satisfy Eq. (11). We call them $\Gamma_{\bar{1}}$, $\Gamma_{\bar{2}}$. We may take

$$A_1^{\bar{1}} = A_1^{\bar{2}} = g, \quad A_2^{\bar{1}} = \Gamma_{\bar{1}} - \Gamma_1, \quad A_2^{\bar{2}} = \Gamma_{\bar{2}} - \Gamma_1 \quad (11.2)$$

and we have

$$(\Gamma_{\bar{1}}, \Gamma_{\bar{2}}) = \bar{\Gamma} = (1/2)(\Gamma_1 + \Gamma_2) \pm [g^2 - (1/4)(\omega_1 - \omega_2)^2]^{1/2}. \quad (11.3)$$

If $|\omega_1 - \omega_2| \gg \gamma$, g the two values of $\bar{\Gamma}$ are Γ_1 , Γ_2 . In this case the nondiagonal matrix element g has no effect. For $|\omega_1 - \omega_2| < 2g$ the imaginary parts of $\Gamma_{\bar{1}}$, $\Gamma_{\bar{2}}$ are equal to each other. In this case one has no effect of the electric field on the emission frequencies $\omega_{\bar{1}}/2\pi$, $\omega_{\bar{2}}/2\pi$. Since $\omega_{\bar{1}} = \omega_{\bar{2}} = (\omega_1 + \omega_2)/2$. If finally $|\omega_1 - \omega_2| \ll 2g$ we may take in addition $\gamma_{\bar{1}} = \gamma + g$, $\gamma_{\bar{2}} = \gamma - g$. For $n=2$, $j=1/2$ in accordance with Table I we have $\gamma = g$ so that $\gamma_{\bar{1}} = 2\gamma$, $\gamma_{\bar{2}} = 0$. This corresponds to the fact that the $2s$ level is metastable. The first effect of the introduction of a weak field is to make

$$\begin{aligned} \gamma_{\bar{2}} &= \gamma - [\gamma^2 - (\omega_1 - \omega_2)^2/4]^{1/2} \cong (\omega_1 - \omega_2)^2/8\gamma \\ \gamma_{\bar{1}} &= \gamma + [\gamma^2 - (\omega_1 - \omega_2)^2/4]^{1/2} \cong 2\gamma. \end{aligned} \quad (11.4)$$

Thus, in agreement with Bethe,⁸ the presence of an electric field destroys the metastability of the $2s$ level gradually and at first in proportion to the square of the electric field.

It is of interest to note that for $|\omega_1 - \omega_2| < 2g$ the observation of radiation from the $n=2$ state does not show the presence of two distinct frequencies ω_1 , ω_2 . Instead there is only one frequency $\bar{\omega} = (\omega_1 + \omega_2)/2$ and two damping constants given by Eq. (11.4). We may say that in this case the coupling of the atom to the radiation is so strong as to make the distinction between the different Stark effect levels meaningless. The state which radiates in accordance with the simple formula $\exp\{-i(\bar{\omega} + i\bar{\gamma})t\}$ is in this case not a stationary state of the matter but a linear combination of two stationary states approaching as a limit either the $2s$ or $2p$ state for $|\omega_1 - \omega_2| \rightarrow 0$.

In the calculation of the polarization of fluorescence radiation we may neglect a factor common to all intensities. We may thus use for the values of K the matrix elements of the coordinates of the absorbing atom instead of the complete expression (1.5). We also omit the factor $(R_{1s}^{3p})^2/9$ which is common to the squares of all the matrix elements. Similarly, instead of the complete B_s entering Eq. (9.1) we use the matrix elements of the coordinates. We calculate first the polarization for the case in which the incident light is polarized with its electric vector parallel to the electric intensity of the field applied to the hydrogen atom. The calculation is conveniently performed separately for $|\omega_2 - \omega_1| > 2g$ and $|\omega_2 - \omega_1| < 2g$. One obtains the same formula for the final answer. We indicate an intermediate step for $x < g$, $x = (\omega_2 - \omega_1)/2$ and for the polarization of the fluorescence radiation parallel to that of

the incident radiation. We have

$$\begin{pmatrix} \kappa(\bar{1}\bar{1}), \kappa(\bar{1}\bar{2}) \\ \kappa(\bar{2}\bar{1}), \kappa(\bar{2}\bar{2}) \end{pmatrix} = [4g^2(g^2 - x^2)]^{-1} \begin{pmatrix} |Z_2|^2, -Z_1^*Z_2 \\ -Z_2^*Z_1, |Z_1|^2 \end{pmatrix} \dots, \tag{12.1}$$

$$\begin{pmatrix} \beta(\bar{1}\bar{1}), \beta(\bar{1}\bar{2}) \\ \beta(\bar{2}\bar{1}), \beta(\bar{2}\bar{2}) \end{pmatrix} = \frac{51}{450}(R_{2p^{3d}})^2 \begin{pmatrix} |Z_1|^2, Z_1^*Z_2 \\ Z_2^*Z_1, |Z_2|^2 \end{pmatrix} + \frac{1}{9}(R_{2s^{3p}})^2 \begin{pmatrix} |Z_2|^2, Z_1^*Z_2 \\ Z_2^*Z_1, |Z_1|^2 \end{pmatrix}, \tag{12.2}$$

where

$$Z_1 = g + (g^2 - x^2)^{1/2} + ix = A_1\bar{1} + A_2\bar{1} = (A_1\bar{2} - A_2\bar{2})^* \tag{12.3}$$

$$Z_2 = g - (g^2 - x^2)^{1/2} - ix = A_1\bar{2} + A_2\bar{2} = (A_1\bar{1} - A_2\bar{1})^*, \tag{12.4}$$

$$x = (\omega_2 - \omega_1)/2, \quad (n, j, m) = (3, 3/2, 1/2). \tag{12.5}$$

Using Z_1, Z_2 as defined by Eqs. (12.3), (12.4), (12.5) but with different values of g, γ, x we have for

$$(n, j, m) = (3, 1/2, 1/2), \tag{13.1}$$

$$\begin{pmatrix} \kappa(\bar{1}\bar{1}), \kappa(\bar{1}\bar{2}) \\ \kappa(\bar{2}\bar{1}), \kappa(\bar{2}\bar{2}) \end{pmatrix} = [4g^2(g^2 - x^2)]^{-1} \begin{pmatrix} |Z_1|^2, -Z_2Z_1^* \\ -Z_1Z_2^*, |Z_2|^2 \end{pmatrix}, \tag{13.2}$$

$$\begin{pmatrix} \beta(\bar{1}\bar{1}), \beta(\bar{1}\bar{2}) \\ \beta(\bar{2}\bar{1}), \beta(\bar{2}\bar{2}) \end{pmatrix} = \frac{1}{18}(R_{2s^{3p}})^2 \begin{pmatrix} |Z_1|^2, Z_1^*Z_2 \\ Z_2^*Z_1, |Z_2|^2 \end{pmatrix} + \frac{1}{6}(R_{2p^{3s}})^2 \begin{pmatrix} |Z_2|^2, Z_1^*Z_2 \\ Z_2^*Z_1, |Z_1|^2 \end{pmatrix}. \tag{13.3}$$

Substituting these values into Eq. (9) we obtain I_z the intensity of the fluorescence radiation polarized along the z axis which we suppose to be parallel to the electric vector of the incident radiation. Similarly one may calculate $I = I_x + I_y + I_z$ and hence I_x as $(I - I_z)/2$. For the degree of polarization $P = (I_z - I_x)/(I_z + I_x)$ we find

$$P = A/(B + C), \tag{14}$$

where

$$A = \{ [(7/50)(R_{2p^{3d}})^2x^2 + (1/6)(2\gamma^2 + 2\gamma g + x^2)(R_{2s^{3p}})^2] \gamma^{-1}(\gamma^2 - g^2 + x^2)^{-1} \}_{j=3/2}, \tag{14.1}$$

$$B = \{ [(141/450)(R_{2p^{3d}})^2x^2 + (5/18)(2\gamma^2 + 2\gamma g + x^2)(R_{2s^{3p}})^2] \gamma^{-1}(\gamma^2 - g^2 + x^2)^{-1} \}_{j=3/2}, \tag{14.2}$$

$$C = \{ [(1/9)(2\gamma^2 - 2\gamma g + x^2)(R_{2s^{3p}})^2 + (1/3)(R_{2p^{3s}})^2x^2] \gamma^{-1}(\gamma^2 - g^2 + x^2)^{-1} \}_{j=1/2}. \tag{14.3}$$

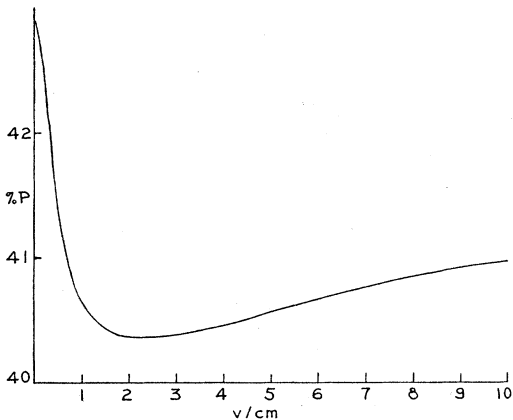


FIG. 2. Polarization of $H\alpha$.

As already mentioned, this result holds for $g < x$ as well as for $g > x$. The fact that the same analytic expression applies whether Eq. (11.3) gives different values of $\bar{\omega}$ or not is due to the continuity in the variation of the radiated spectrum with the electric field. The way in which P depends on the electric field is shown in Fig. 2.

It should be noted that in the geometrical arrangement to which Eq. (14) applies the $\kappa(\bar{b}\bar{b}')$ are diagonal with respect to m and that we have neglected the matrix elements between states with same m but different j . We are justified in doing so because the levels with different j are separated by appreciably more than the natural breadths. The values of the separations and half value widths are:

$W(5/2) - W(3/2) = 0.036 \text{ cm}^{-1}$; $W(3/2) - W(1/2) = 0.108 \text{ cm}^{-1}$; $\gamma(5/2)/\pi = 1/2\pi\tau(5/2) = 0.00018 \text{ cm}^{-1}$; $\gamma(3/2)/\pi = 0.00068 \text{ cm}^{-1}$; $\gamma(1/2)/\pi = 0.00053 \text{ cm}^{-1}$. The change in polarization with the field calculated here is thus due entirely to the radiation coupling between Stark effect levels with the same m and j .