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Interference Effects in the Resonance Fluorescence of "Crossed" Excited Atomic States*

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The recent spectroscopic method developed by Colegrove, Franken, Lewis, and Sands exploits interference effects which occur in the resonance fluorescence of atoms exhibiting pairs of "crossed" excited states. Some of the theoretical features of the technique are discussed in terms of the formalism developed by Breit from which the salient features of the observed lineshapes can be readily deduced. Alternative derivations of the Breit formula are given together with a discussion of the nature and representation of the requisite resonance radiation.

INTRODUCTION

A SPECTROSCOPIC method which exploits interference effects in the resonance scattering from "crossed" excited atomic states has recently been developed[1] and applied to the measurement of helium $2\,^3P$ fine structure[1] and the hyperfine structure of the $^3P_1$ state of Hg^{199}.[2] It is the purpose of this report to discuss some of the theoretical features of the technique with particular attention to lineshape problems and the nature of the requisite resonance radiation.

I. A BRIEF DESCRIPTION OF THE METHOD AND RELATED PHENOMENA

Consider an atom (Fig. 1) having one or more ground-state Zeeman levels a and a group of excited states containing, among others not shown, the two levels b and c which are split in zero magnetic field due to fine or hyperfine interactions and which "cross" at some particular field. It is assumed that these excited states are connected to the ground state by an allowed electric dipole transition so that the phenomenon of resonance fluorescence can occur.

A vapor of these atoms is placed in a cell situated in the apparatus shown in Fig. 2. A spectroscopic lamp projects a beam of the necessary resonance radiation through the cell which is situated in a homogeneous and variable magnetic field. A photodetector is placed as shown and can be monitored by a cathode-ray oscilloscope (CRO).

If the magnetic field is now set at that value where the two levels b and c cross, it is found that more light is received by the detector as shown in the CRO insert of Fig. 2. (A decrease can also be observed depending on the atom, the light polarization if any, and the geometry.) The "width" of this effect is comparable to the natural linewidth of the excited states.

The gist of the phenomenon is discussed in reference 1 and will be summarized at this point. We are interested in writing the expression for the rate $R(\mathbf{f},\mathbf{g})$ at which photons of polarization $\mathbf{f}$ are absorbed and photons of polarization $\mathbf{g}$ are re-emitted by the atoms in the resonance fluorescence process. Assuming that the resonance radiation from the lamp is sufficiently broad, the expression for R when the levels b and c are completely resolved is given by

$$R_{\text{resolved}} \sim |f_{ab}g_{ba}|^2 + |f_{ac}g_{ca}|^2, \tag{1a}$$

where $f_{ab}=(a|\mathbf{f}\cdot\mathbf{r}|b)$, $g_{ba}=(b|\mathbf{g}\cdot\mathbf{r}|a)$, etc. The expression for R when the levels b and c are completely unresolved (crossed) is given by

$$R_{\text{crossed}} \sim |f_{ab}g_{ba}+f_{ac}g_{ca}|^2. \tag{1b}$$

The expressions (1a) and (1b) are identical if any of the matrix elements vanish, i.e., the interference effect vanishes unless the two levels are able to "share" photons of polarization $\mathbf{f}$ and $\mathbf{g}$. This is analogous to the classical phenomenon of double-slit interference patterns where it is said that the same photon can be shared by both slits. Furthermore, it is found that the total

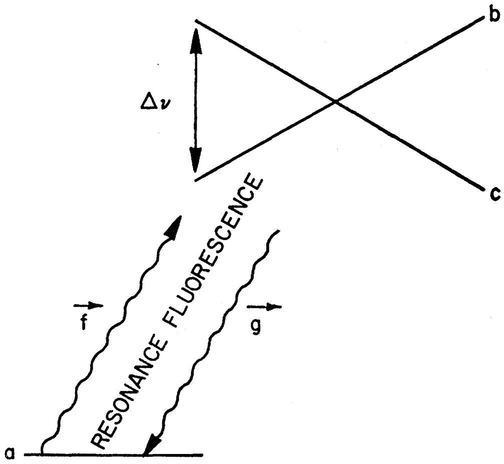

FIG. 1. Energy level diagram. The excited states b and c, among others not shown, are separated in zero magnetic field by the amount $\Delta\nu$ due to fine or hyperfine structure interactions and cross at some specific value of the field. In the resonance fluorescence process, photons of polarization $\mathbf{f}$ are absorbed and those of polarization $\mathbf{g}$ are re-emitted.

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

[2] H. R. Hirsch, Bull. Am. Phys. Soc. 5, 274 (1960).

absorption cross section for the resonance radiation is independent of whether the levels are crossed; the only effect of the crossing is to modify the angular distribution of the re-emitted radiation. The double-slit analogy is simply that the same amount of light (number of photons per second) goes through the slits whether they are close together or well resolved; the only effect produced when the slits are close (apart from possible geometric factors) is the modification of the distribution of light intensity on the display screen.

The interference phenomenon exhibited in this experiment on atoms is intimately related to the effects produced by degeneracy in the intermediate state of a gamma-gamma cascade in which angular correlation is studied.[3] Similar interference effects also play a predominant role in the "light beat" experiments of Series *et al.*[4] in which a radio-frequency modulation of the resonance fluorescence can be observed upon the application of specific radio-frequency magnetic fields to the absorbing atoms.

The exploitation of this phenomenon for the precision spectroscopy of excited atomic states[1,2] rests upon the fact that the magnetic field at which pairs of levels cross can be determined accurately and hence the zero-field splittings can be estimated, provided the field dependence of the levels is known. As a spectroscopic method the technique is analogous to the double-resonance method of Brossel *et al.*[5] in which changes in the angular distribution of resonance fluorescence are achieved by "mixing" two excited states together by the action of a radio-frequency magnetic field that satisfies the resonance condition for the energy separation. In the present method no radio-frequency field is required because the energy separation at crossing is zero and the "mixing" becomes simply an intimate part of the radiation process itself.

Finally, it should be noted that the interference phenomenon of the present method has already been studied in much detail for the case of zero or low magnetic fields where the several Zeeman levels in a typical excited state become degenerate, i.e., a special case of crossing. This zero-field crossing gives rise to changes in the polarization and angular dependence of the resonance fluorescence and is usually referred to as the Hanle effect.[6]

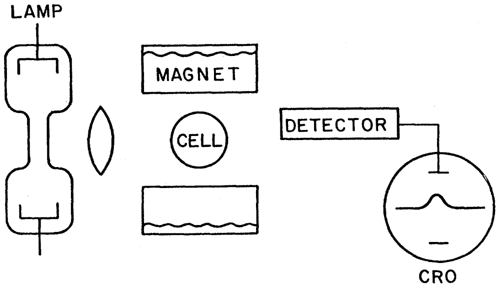

FIG. 2. Schematic diagram of the apparatus discussed in the text.

II. THE BREIT FORMULA

The expressions for R given in Eqs. 1(a) and 1(b) suffice for the calculation of many experimental parameters such as the magnitude of the interference effect, its directional sensitivity, polarization conditions for optimum sensitivity, etc.[7] However, these equations do not give any information about the interference other than at its extremes; i.e., at complete crossing and at complete separation of the excited states. The in-between region requires a more detailed treatment of the resonance fluorescence process that yields information about the lineshape as well as Eqs. (1) in appropriate limits.

A. Discussion of the Pulse Excitation

Breit[8] has derived an expression for the resonance fluorescence under pulse excitation for atoms exhibiting partial or complete degeneracy in the excited states. (A simple derivation of this formula is given in Appendix 1.) Consider a lamp containing atoms (called source atoms) of the same type as the atoms in the cell (called sample atoms). At $t=t_0$ a source atom is an excited state and the sample atom is in the ground state. The sample atoms will be assumed to have a decay rate, when excited, of Γ sec^{-1} (mean lifetime of $1/\Gamma$ seconds). The source atoms are assumed to have a decay rate of γ sec^{-1}. The pulse excitation process is realized if γ is allowed to become very large. That is, the source atom decays so abruptly that it emits light having a very broad range of spectral frequencies and the excitation of the sample atom occurs in a time very short compared with times characteristic of the fluorescence process. Most importantly, this type of excitation has the distinct characteristic of *coherent* excitation of the sample atom; i.e., if the light emitted from the source atom has a polarization such that two levels of the sample atom can be excited, then these levels are *excited coherently with this one pulse even if the levels are completely resolved.*

A more realistic model for a lamp does not exhibit

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[3] See, for example, L. C. Biedenharn and M. E. Rose, Revs. Modern Phys. 25, 729 (1953).

[4] J. N. Dodd, W. N. Fox, G. W. Series, and M. J. Taylor, Proc. Phys. Soc. (London) 74, 789 (1959). The theory of these effects will be submitted shortly to Proc. Phys. Soc. by Dodd and Series. [G. W. Series (private communication)].

[5] J. Brossel and A. Kastler, Compt. rend. 229, 1213 (1949); and J. Brossel and F. Bitter, Phys. Rev. 86, 308 (1952).

[6] See, for example, A. C. G. Mitchell and M. W. Zemansky, *Resonance radiation and excited atoms* (Cambridge University Press, New York, 1934), Chap. V.

[7] While preparing this manuscript the author has learned that M. E. Rose and R. Carovillano have prepared a more general formulation of the angular dependence of the interference effects and performed a detailed analysis of the interference effects to be expected in atomic hydrogen. This material will be published shortly [M. E. Rose and R. R. Lewis (private communication)].

[8] G. Breit, Revs. Modern Phys. 5, 91 (1933); see particularly pp. 117–125.

this pulse characteristic. Specifically, the lamp contains atoms having decay rates comparable to the decay rate of the sample atoms and the broad frequency spectrum of the lamp comes about because the emitting atoms exhibit a broad range of Doppler shifts. For this case two resolved excited states of the sample atom would not be excited coherently; i.e., these two excited states could not be excited with the photon emitted from one of the source atoms since that light could no longer have Fourier components available for both excitations. These two states could be excited coherently only if they were separated by less than approximately γ sec^{-1} or Γ sec^{-1}, whichever is larger. We might thus expect that the range in the excited state separation in which interference effects would be appreciable might be sensitive to the magnitude of the source-atom decay rate γ, and that therefore the Breit formula would only be an approximation to actual experimental conditions.

In order to examine this possibility we have generalized the calculation to include arbitrary decay rates in the source atoms, which calculation includes Breit's pulse limit, and find that the interference effects in the resonance fluorescence are actually independent of the decay rate. (This more general calculation is described in Appendix II.) It can be argued that this result could be anticipated from the fact that the density matrix describing weak radiation fields is independent of whether sharp wave packets at random times (pulses) or a spread of monochromatic waves of random phases are supposed.[9]

It is important to note, however, that for the situation of strong radiation fields (i.e., classical fields) one can construct experiments that do distinguish between these two models. The essential feature of the strong field is that there are enough photons present in particular modes to permit the simultaneous specification of phase and amplitude as, for example, in the case of a microwave cavity. In the present experiment, as in all experiments dealing with conventional sources, the light beam contains much less than one photon per mode in the appropriate frequency interval and must therefore be considered as a weak field.[10] The derivation of the Breit formula given in Appendix II does treat the radiation field calssically but nevertheless yields the correct weak-field result.

B. The Application of Breit's Formula to the Crossed-Level Technique

The Breit formula treats the general case of an atom having one or more ground-state levels m, m', etc., and a group of excited states μ, μ', etc., which may exhibit partial or complete degeneracy (crossings). The expression gives the rate $R(\mathbf{f},\mathbf{g})$ at which photons of polarization $\mathbf{f}$ are absorbed and photons of polarization $\mathbf{g}$ are re-emitted in the resonance fluorescence process:

$$R(\mathbf{f},\mathbf{g})=c\sum_{\mu\mu'mm'}\frac{f_{\mu m}f_{m\mu'}g_{\mu'm'}g_{m'\mu}}{1-2\pi i\tau\nu(\mu,\mu')},\qquad(2)$$

where $f_{\mu m}=(\mu|\mathbf{f}\cdot\mathbf{r}|m)$, etc.; τ is the mean lifetime of each excited state; $\nu(\mu,\mu')=(E_\mu-E_{\mu'})/h$; c is a parameter proportional to the intensity of the lamp, geometrical factors, etc.

For the case where the excited states are completely resolved, $2\pi\tau\nu(\mu,\mu')\gg1$ for all values of $\mu\neq\mu'$ and Eq. (2) reduces to

$$R(\mathbf{f},\mathbf{g})=R_0=c\sum_{\mu mm'}|f_{\mu m}|^2|g_{\mu m'}|^2.$$

This is just the resonance fluorescence rate without any interference terms. Interference effects occur when two or more of the excited states are close enough together so that $2\pi\tau\nu(\mu,\mu')\lesssim1$.

In order to exhibit the features of this interference let us specialize to a system containing only one ground state, a, and two excited states b and c (Fig. 1). When the two excited states b and c are well resolved, then Eq. (2) becomes

$$R(\mathbf{f},\mathbf{g})=R_0=|f_{ab}|^2|f_{ba}|^2+|g_{ac}|^2|g_{ca}|^2.$$

When the states b and c are "close," then Eq. (2) becomes

$$R(f,g)=R_0+\frac{A}{1-2\pi i\tau\nu(b,c)}+\frac{A^*}{1+2\pi i\tau\nu(b,c)}\equiv R_0+S,\quad(3)$$

where $A=f_{ba}f_{ac}g_{ca}g_{ab}$. For convenience the signal term

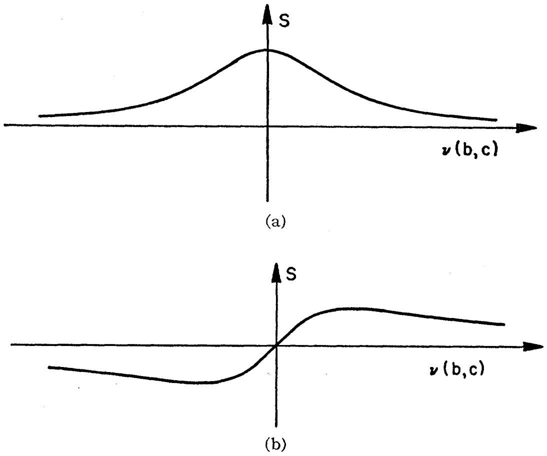

FIG. 3. The strength of the interference signal S [Eq. (4)] as a function of the excited state splitting $\nu(b,c)$. Figure 3(a) is the Lorentz lineshape which occurs when the matrix product A is real. Figure 3(b) is the lineshape which is found when A is pure imaginary.

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[9] See, for example, R. H. Dicke and J. P. Wittke, *Introduction to Quantum Mechanics* (Addison Wesley Publishing Company, Reading, Massachusetts, 1960), pp. 336–337. I am indebted to R. H. Dicke, E. W. Johnston, and E. M. Purcell for several valuable discussions about this and related points.

[10] In a strong beam of resonance radiation the number of photons per mode in the appropriate frequency range is $\sim10^{-4}$. It is for this reason that the rate of absorption of resonance radiation per atom in such beams is some four orders of magnitude less than the rate of spontaneous emission.

S can be written

$$S=\frac{A+A^*}{1+4\pi^2\tau^2\nu^2(b,c)}+\frac{(A-A^*)2\pi i\tau\nu(b,c)}{1+4\pi^2\tau^2\nu^2(b,c)}. \tag{4}$$

For the case where the matrix product A is real, then S is just the well-known Lorentz lineshape [see Fig. 3(a)] with full half-width $\Delta\nu(b,c)=1/\pi\tau$. This width is just twice the natural width of each excited state.

For the case where the matrix product A is pure imaginary, S becomes

$$S=\frac{4\pi i A\tau\nu(b,c)}{1+4\pi^2\tau^2\nu^2(b,c)}. \tag{5}$$

This line shape is shown in Fig. 3(b). If the matrix product A is complex, then it is possible to have a mixture of the two pure forms shown in Fig. 3. The conditions for which A is real, imaginary, or complex depends on the direction and polarization of the incoming and outgoing beams of light. In general, all three cases can be realized experimentally.

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It is a pleasure to thank J. N. Dodd, R. R. Lewis, M. E. Rose, G. W. Series, and R. H. Sands for their very helpful contributions. I want particularly to acknowledge the enormous benefit of many discussions I enjoyed with Willis Lamb during the fall of 1959, and the many courtesies extended to me by the Clarendon Laboratory, Oxford.

APPENDIX 1. A SIMPLE DERIVATION OF THE BREIT FORMULA UNDER CONDITIONS OF PULSE EXCITATION

The sample atom is considered to have a set of ground states m, m', etc. and a set of excited states μ, μ', etc., which may exhibit partial or complete degeneracy. The sample atom will be exposed to a series of pulses of polarization $\mathbf{f}$ occuring at random times and far enough apart so that any process arising from the action of one pulse is finished before the arrival of the next. It is furthermore assumed that each pulse contains the Fourier components necessary for any of the possible absorptions from any ground state m to any excited state μ and that the duration of the pulse is short compared to the reciprocal of any of the frequency differences in the excited states. (These two conditions are clearly related.)

At the time $t=0$ the atom is assumed to be in some particular ground state m,[11] the energy of which, for convenience, is taken to be zero. Thus the wave function for the atom before the pulse is $\Psi_0=u_m$. At $t=0$ the atom is subjected to the pulse and the wave function from that time on is given by

$$\Psi(t>0)=u_m+\textstyle\sum_\mu f_{m\mu}u_\mu e^{-(i\omega_\mu+\frac{1}{2}\Gamma)t}. \tag{I,1}$$

The amplitude of the ground state m is still taken as unity because this is a first order calculation. The fact that the initial excited state amplitudes are given simply by the matrix elements $f_{m\mu}$ follows as a consequence of the brevity of the pulse. The subsequent radiation damping of the excited states is accounted for by the inclusion of the factor $\exp(-\frac{1}{2}\Gamma t)$. (The uninteresting constants of proportionality have been set equal to unity in this and in the following expressions.)

The instantaneous rate at which a photon of polarization $\mathbf{g}$ is emitted by the excited atom is given by

$$\begin{aligned}R(\mathbf{f},\mathbf{g},t)&=\sum_m\sum_{m'}|(\Psi^*|\mathbf{g}\cdot\mathbf{r}|u_{m'})|^2\\&=\sum_{\mu\mu'mm'}f_{\mu m}f_{m\mu'}g_{\mu'm'}g_{m'\mu}e^{[2\pi i\nu(\mu,\mu')-\Gamma]t},\end{aligned} \tag{I,2}$$

where $2\pi\nu(\mu,\mu')=\omega_\mu-\omega_{\mu'}$ and the additional summation over m has been introduced because the initial ground state could have been any one of the set m.

If, now, the atom is subjected to N pulses (photons) per second, well separated in time, then the rate $R(\mathbf{f},\mathbf{g})$ at which photons of polarization $\mathbf{f}$ are absorbed and $\mathbf{g}$ are re-emitted is given by

$$\begin{aligned}R(\mathbf{f},\mathbf{g})&=N\int_0^\infty R(\mathbf{f},\mathbf{g},t)dt\\&=N\sum_{\mu\mu'mm'}\frac{f_{\mu m}f_{m\mu'}g_{\mu'm'}g_{m'\mu}}{\Gamma-2\pi i\nu(\mu,\mu')}.\end{aligned} \tag{I,3}$$

This expression is identical with the Breit formula, Eq. (2), since $\Gamma=1/\tau$.

APPENDIX II. THE DERIVATION OF THE BREIT FORMULA WITHOUT THE CONDITION OF PULSE EXCITATION

We shall follow the form of the derivation given in the preceding Appendix as much as possible. The decay constant of the source atoms γ and the decay constant of the sample atoms Γ will have arbitrary values. The source atoms are assumed to be excited and emit resonance radiation at random times (incoherently) and with random central frequencies (Doppler-broadened "white" light). Both of these assumptions are excellent for the lamp intensities usually employed in these experiments.

At $t=0$ we consider an excited source atom and a sample atom that is in a particular ground state $u_m(r)$,[11] the energy of which is taken to be zero. The state of the sample atom will be described at all times by

$$\begin{aligned}&\Psi=u_m, \quad t<0\\&\Psi=\textstyle\sum_\mu a_\mu(t)u_\mu+b_m(t)u_m, \quad t\geqslant 0.\end{aligned} \tag{II,1}$$

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[11] This simplification is valid only for those experiments in which there is no preferred occurrence of specific configurations of the ground states m.

The sample atom experiences an electric field **E**, for $t \geqslant 0$, due to the decay of the source atom:

$$\mathbf{E} = \mathbf{f}E_0 \cos\omega t e^{-\frac{1}{2}\gamma t}$$
$$= \mathbf{f}(E_0/2)e^{-i\omega t - \frac{1}{2}\gamma t},$$

where **f** is the polarization, ω is the central angular frequency of emission, and the rotating wave approximation has been employed.

The Hamiltonian is $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$, where $\mathcal{H}_0$ is the complete Hamiltonian for the atom including the effects of all static electromagnetic fields and $\mathcal{H}' = e\mathbf{E}\cdot\mathbf{r}$.

The Schrödinger equation is

$$\dot{a}_\mu = -i\omega_\mu a_\mu + \frac{1}{ih}\sum_{\mu'} \mathcal{H}_{\mu\mu'}' a_{\mu'}(t) + \frac{1}{ih}\mathcal{H}_{\mu m}' b_m(t) - \tfrac{1}{2}\Gamma a_\mu,$$

where the term $-\frac{1}{2}\Gamma a_\mu$ has been added to account for the radiation damping of the excited states. The $\sum_{\mu'}$ term vanishes identically for all cases where the excited states have the same L value, and yields a negligible contribution otherwise. Since this is a first order calculation, we set $b_m(t) = 1$ for all times. Thus:

$$\dot{a}_\mu = B_\mu e^{-i\omega t - \frac{1}{2}\gamma t} - (\tfrac{1}{2}\Gamma + i\omega_\mu)a_\mu, \qquad \text{(II,2)}$$

where $B_\mu = (eE_0/2ih)(\mu|\mathbf{f}\cdot\mathbf{r}|m)$. Taking the boundary condition $a_\mu = 0$ at $t = 0$, the integration of (II,2) yields:

$$a_\mu(t) = B_\mu e^{-(\frac{1}{2}\Gamma + i\omega_\mu)t}\left[\frac{e^{i(\omega_\mu - \omega)t - \lambda t} - 1}{i(\omega_\mu - \omega) - \lambda}\right], \qquad \text{(II,3)}$$

where $\lambda = \frac{1}{2}\gamma - \frac{1}{2}\Gamma$.

The instantaneous rate at which a photon of polarization **g** is emitted by the excited atom is given by

$$R(\mathbf{f},\mathbf{g},t) = \textstyle\sum_{m'} \left|\left(\sum_{\mu'} a_{\mu'}(t) u_{\mu'}|\mathbf{g}\cdot\mathbf{r}|u_{m'}\right)\right|^2. \qquad \text{(II,4)}$$

In order to find the rate $R(\mathbf{f},\mathbf{g})$ at which photons of polarization **f** are absorbed and **g** re-emitted for a "white" beam of incoming photons, we must first integrate (II,4) over t from 0 to ∞, then integrate ω from $-\infty$ to $+\infty$, and finally sum over all ground states m. It should be noted that the integration over time in this simple way is valid only for cases where the incoming light beam is weak enough so that each sample atom undergoes the entire resonance fluorescence process in a time short compared with the mean time between fluorescence events for this atom.[10] Combining (II,3) and (II,4) under the required integration yields:

$$R = \frac{e^2E_0^2}{4\hbar^2}\sum_{\mu\mu'mm'} f_{m\mu'}f_{\mu m}g_{m'\mu}g_{\mu'm'}$$
$$\times\int_0^\infty dt\int_{-\infty}^\infty d\omega\frac{e^{-i\omega_{\mu\mu'}t - \Gamma t}}{[(\omega_\mu - \omega) + i\lambda][(\omega_{\mu'} - \omega) - i\lambda]}$$
$$\times[e^{+i\omega_{\mu\mu'} - 2\lambda t} - e^{i(\omega_\mu - \omega)t - \lambda t} - e^{-i(\omega_{\mu'} - \omega)t - \lambda t} + 1]. \qquad \text{(II,5)}$$

The integral over ω yields readily to contour integration owing to the simple singularities at $\omega_\mu + i\lambda$ and $\omega_{\mu'} - i\lambda$, and the integration over time is straightforward. The result is:

$$R(f,g,t) = \left(\frac{e^2E_0^2}{4\hbar^2}\right)\left(\frac{2\pi}{\gamma}\right)\sum_{\mu\mu'mm'}\frac{f_{m\mu'}f_{\mu m}g_{m'\mu}g_{\mu'm'}}{\Gamma - i\omega(\mu,\mu')}. \qquad \text{(II,6)}$$

This expression is identical with the Breit formula, Eq. (2), since $\Gamma = 1/\tau$ and $\omega(\mu,\mu') = 2\pi\nu(\mu,\mu')$. The factor $2\pi/\gamma$ actually plays no role since the normalization over the light pulse (one photon condition) requires E_0^2/γ to be independent of γ.