

Theory of Collision Broadening in the Sudden Approximation*

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A method is developed for calculating the cross section for line broadening in the limiting case in which important collisions may be considered to occur very rapidly with respect to the periods corresponding to the transitions in question. This method is essentially an extension of the familiar "sudden" approximation; reference is made throughout to the particular example of optical double resonance only for definiteness and because there are available experimental results for comparison with the theory. Assuming the impact model and considering the case when the energy levels in question are well resolved with respect to their width, an exact expression is found for resonant self-broadening in the usual weak rf field limit of interest in double resonance. For the case of very small oscillator strengths for the *optical* transition (intercombination lines), the resonant broadening becomes sufficiently small so that second-order, intermediate-state processes dominate, and approximations must be made to effect sums over intermediate states. Here the broadening is of the same sort as foreign gas broadening, and in many cases of interest, the approximations can be made in a sufficiently realistic manner to obtain useful expressions for the broadening. It is shown that the resonant cross section and this "second-order" cross section are *not* additive, but that the one which is larger dominates the total cross sections very strongly. Finally, we evaluate explicitly the self-broadening and foreign gas broadening (by the noble gases) of double resonance lines in the group II metals and the self-broadening in the optical spectrum of helium. In all cases our theoretical predictions are in good agreement with measurements which have been made.

I. INTRODUCTION

THE purpose of this paper is to develop a quantitative theory of pressure broadening in the "sudden" approximation with application to the case of optical double resonance lines. There are at present several observations of the increase of double resonance linewidths with density for self-broadening in zinc¹ and in cadmium,² and for foreign gas broadening in mercury.³ In the case of zinc a rather severe disagreement has been found between the observed cross section for broadening and theoretical estimates based on the theories of Furssov and Vlassov⁴ and others.⁵ In this work, this discrepancy is explained and explicit formulas are obtained for self-collision broadening both in the limit of large and small oscillator strengths of the optical transition. Formulas are also derived for foreign gas broadening in the interesting case of broadening by the noble gases. In Sec. II the theoretical expression for the line shape in the presence of collisions is derived, and in

Sec. III some specific cases are calculated for the purpose of comparison with experiment.

II. GENERAL THEORY

The problem under consideration is the broadening of resonance lines resulting from radio-frequency-induced transitions between the magnetic sublevels of an atomic state, where change of polarization of the emitted *optical* radiation is used as a detector. The problem of these transitions, neglecting collisions, in the case of equal spacing of the levels was solved exactly by the well-known result of Majorana⁶ which gives the probability $P(t)$, that an atom initially in the state (F, m) will at a later time t , find itself in the state (F, m') under the influence of an rf magnetic field \mathbf{B}_1 , of frequency ω . The magnetic sublevels are assumed to be spaced equally due to the presence of a weak static magnetic field \mathbf{B}_0 , which produces level separations $\hbar\omega_0$. The analysis required to obtain the Majorana formula is rather complicated, and if the complication of perturbing collisions is added an exact solution is out of the question. However, since the excited states involved usually have lifetimes τ which are quite short (typically of order one microsecond), the radio-frequency field can act on the atom only a very short time, so that if the field is very weak, i.e., $\gamma_F B_1 \ll 1/\tau$, the probability of transition to any but the nearest magnetic sublevel can be ignored. $\gamma_F B_1$ is just the familiar "flipping frequency."

In the case $\gamma_F B_1 \ll 1/\tau$, we may consider the problem of transitions between m and $m+1$ as an isolated two-level problem. Although the simple two-

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¹ M. Dumont, thèse de troisième cycle, Ecole Normale Sup. Paris, 1962 (unpublished).

² F. W. Byron, Jr., thesis, Columbia University, 1963 (unpublished).

³ C. A. Piketty-Rives, diplôme d'études supérieures, Ecole Normale Sup. Paris, 1960 (unpublished).

⁴ V. Furssov and A. Vlassov, *Physik Z. Sowjetunion* **10**, 378 (1938).

⁵ See, for example, R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon Press, Inc., New York, 1961).

⁶ E. Majorana, *Nuovo Cimento* **9**, 43 (1930).

level flipping formula is readily obtained exactly, it is instructive to examine it via perturbation theory since when the effect of collisions is introduced a straightforward solution of the resulting Schrödinger equation is not possible. For the two-level problem, $P(t)$ is given by (keeping only through lowest order in $\gamma_F B_1$)

$$P(t) = (F-m)(F+m+1) \frac{\sin^2 \frac{1}{2}(\omega - \omega_0)t}{(\omega - \omega_0)^2} (\gamma_F B_1)^2,$$

which is to be compared with the exact expression

$$P(t) = (F-m)(F+m+1) \frac{(\gamma_F B_1)^2}{(\gamma_F B_1)^2 + (\omega - \omega_0)^2} \times \sin^2 \frac{1}{2} [(\omega - \omega_0)^2 + (\gamma_F B_1)^2]^{1/2} t.$$

For t sufficiently small, the two expressions agree. To obtain the double resonance line shape $I(\omega)$, this probability must be weighted by the probability of decay to the ground state of the atom, $(1/\tau)e^{-t/\tau}$, and integrated from zero to infinity to account for the finite lifetime of the excited state.⁷ In the first (perturbation theory) case

$$I(\omega) = \frac{1}{2}(F-m)(F+m+1) \frac{(\gamma_F B_1)^2}{(1/\tau)^2 + (\omega - \omega_0)^2}, \quad (1)$$

and in the second (exact) case

$$I(\omega) = \frac{1}{2}(F-m)(F+m+1) \times \frac{(\gamma_F B_1)^2}{(1/\tau)^2 + (\gamma_F B_1)^2 + (\omega - \omega_0)^2}, \quad (2)$$

apart from a factor giving the density of excited atoms. Because of our decision to neglect $\gamma_F B_1$ with respect to $1/\tau$, these two results agree also.

To summarize, throughout this work it will be assumed that $\gamma_F B_1 \ll 1/\tau$, and the two levels involved are considered to be isolated. The smallness of $\gamma_F B_1$ will be used to neglect all but the lowest contributing order in time-dependent perturbation theory.

Consider the Hamiltonian, $H = H_0 + H_c(t) - \mathbf{u} \cdot \mathbf{B}_1$, where \mathbf{u} is the magnetic dipole moment of the system in question. H_0 is the unperturbed Hamiltonian of two atoms in a static magnetic field, one in the excited state, the other, which will be called the perturbing atom, in the ground state. $H_c(t)$ represents the effect of the interaction between the atoms, containing the usual dipole-dipole, dipole-quadrupole, etc., terms of the multipole expansion of the interaction between two electrically neutral atoms. The two atoms are considered as colliding repeatedly with each other in an uncorrelated way to simulate the effect of many perturbers on the excited atom. This term, which must be defined statistically, will be referred to as the collision Hamiltonian. With

$\mathbf{B}_1 = B_1(\mathbf{i} \cos \omega t + \mathbf{j} \sin \omega t)$, the expression for H may be written as

$$H = H_0 + H_c(t) - \frac{1}{2} B_1 [\mu_+ e^{-i\omega t} + \mu_- e^{i\omega t}],$$

where $\mu_{\pm} = \mu_x \pm i\mu_y$. Since $\mathbf{u} = \gamma_F \mathbf{F}$, where \mathbf{F} is the total angular momentum of the excited atom, μ_+ and μ_- correspond to the usual raising and lowering operators for magnetic sublevels, and hence to annihilation and creation of radio-frequency quanta. This last term will be referred to as H_{pf} for the interaction of the particles with the field. The solutions of H_0 are assumed to be known,

$$i\hbar(\partial\psi_n/\partial t) = H_0\psi_n,$$

where n stands for a member of a complete set of quantum numbers. Define $H_p = H_0 + H_c(t)$; $U_p(t, t_0)$ will be the corresponding time-development operator satisfying the equation $i\hbar\dot{U}_p(t, t_0) = H_p U_p(t, t_0)$ with the requirement that $U_p(t_0, t_0) = 1$. Similarly, $U_0(t, t_0)$ corresponds to H_0 and $U(t, t_0)$ corresponds to H . We want the probability that an atom, initially in the state n , will find itself at a later time T , in the state m . This will be given by

$$\begin{aligned} P &= |\langle \psi_m(T) | U(T, t_0) | \psi_n(t_0) \rangle|^2, \\ &= |\langle U_p^{-1}(T, t_0) \psi_m(T) | U_p^{-1}(T, t_0) U(T, t_0) | \psi_n(t_0) \rangle|^2, \\ &= |\langle \psi_m(t_0) | U_p^{-1}(T, t_0) U(T, t_0) | \psi_n(t_0) \rangle|^2. \end{aligned}$$

At this point the utility of the interaction representation is evident. Calling $U_p^{-1}U = V$, $i\hbar\dot{V} = (U_p^{-1}H_{pf}U_p)V$ which may be solved by iteration, $V = V_0 + V_1 + V_2 + \dots$, where

$$V_0 = 1, \quad V_1 = -\frac{i}{\hbar} \int_{t_0}^T U_p^{-1}(t', t_0) H_{pf}(t') U_p(t', t_0) dt',$$

and so forth. Clearly, V_0 gives no contribution. Hence to lowest order in B_1 ,

$$P = \frac{1}{\hbar^2} \left| \int_{t_0}^T \langle \psi_m(t_0) | U_p^{-1}(t, t_0) H_{pf}(t) U_p(t, t_0) | \psi_n(t_0) \rangle dt \right|^2,$$

where H_{pf} is as defined above. Consider the case of absorption first. Then only μ_+ will contribute and

$$P = \frac{B_1^2}{4\hbar^2} \left| \int_{t_0}^T \langle \psi_m(t_0) | U_p^{-1}(t, t_0) \mu_+ U_p(t, t_0) | \psi_n(t_0) \rangle e^{-i\omega t} dt \right|^2.$$

Since $U_p^{-1}(t, t_0) \mu_+ U_p(t, t_0) = \mu_+(t)$,

$$\begin{aligned} P &= \frac{B_1^2}{4\hbar^2} \left| \int_{t_0}^T \langle \psi_m(t_0) | \mu_+(t) | \psi_n(t_0) \rangle e^{-i\omega t} dt \right|^2, \\ &= \frac{B_1^2}{4\hbar^2} \int_{t_0}^T dt \int_{t_0}^T dt' \langle n | \mu_-(t) | m \rangle \langle m | \mu_+(t') | n \rangle e^{i\omega t} e^{-i\omega t'}, \\ &= \frac{B_1^2}{4\hbar^2} \int_{t_0}^T dt \int_{t_0}^T dt' e^{i\omega(t-t')} \langle n | \mu_-(t) | m \rangle \langle m | \mu_+(t') | n \rangle. \end{aligned}$$

⁷ J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952).

After summing over all final states, the observed signal is found to be

$$I(\omega) = \frac{B_1^2}{4\hbar^2} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega(t-t')} \langle n | \mu_-(t) \mu_+(t') | n \rangle. \quad (3)$$

To average over initial states, the density matrix is used to obtain

$$I(\omega) = \frac{B_1^2}{4\hbar^2} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega(t-t')} \times \text{Tr}[\rho(t_0) \mu_-(t) \mu_+(t')], \quad (4)$$

where a constant which gives the rate of excitation of the atoms under observation is omitted. In Eq. (3) the limits of integration have been extended to infinity, using the fact that due to both collisions and radiative damping, a constant rate of absorption will ensue. Equation (4) is the generalization of the classical quantum theory result for electric dipole spontaneous radiation, which is the starting point for most discussions of line shape.⁸ In this case there is a quadratic dependence on B_1 as is expected.

Since

$$U_p(t, t_0) \rho(t_0) U_p^{-1}(t, t_0) = \rho(t)$$

and

$$U_p(t, t_0) U_p^{-1}(t', t_0) = U_p(t, t'),$$

$$I(\omega) = \frac{B_1^2}{4\hbar^2} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega(t-t')} \times \text{Tr}[\rho(t) \mu_-(t_0) U_p^{-1}(t', t_0) \mu_+(t_0) U_p(t', t)].$$

The same method which led to the introduction of V above now reduces the problem to a treatment of the collision term only. If $T = U_0^{-1} U_p$, T will then obey the differential equation $i\hbar \dot{T} = (U_0^{-1} H_c U_0) T$. Precisely the same manipulations as above, along with the change of variables $t' = t + \tau$, $t = t$ leads to the expressions,

$$I(\omega) = \frac{B_1^2}{4\hbar^2} \sum_{c,d} \int_{-\infty}^{\infty} e^{-i(\omega - \omega_{cd})\tau} \phi_{cd}(\tau) d\tau, \quad (5a)$$

$$\phi_{cd} = \sum_{a,b} \int_{-\infty}^{\infty} \langle a | \rho(t) | a \rangle \langle a | \mu_- | b \rangle \langle b | T^{-1}(t+\tau, t) | c \rangle \times \langle c | \mu_+ | d \rangle \langle d | T(t+\tau, t) | a \rangle dt, \quad (5b)$$

where intermediate states have been inserted and $\rho(t)$

has been taken diagonal, assuming that the effect of collisions will rapidly destroy any coherence (off-diagonal terms). ϕ_{cd} is the correlation function of Anderson⁹ upon whose work this discussion is based. It is easy to see that $\phi_{cd}(-\tau) = \phi_{cd}^*(\tau)$ and, therefore,

$$I(\omega) = \frac{B_1^2}{2\hbar^2} \sum_{c,d} \text{Re} \int_0^{\infty} e^{-i(\omega - \omega_{cd})\tau} \phi_{cd}(\tau) d\tau$$

and only positive values of τ will be considered in what follows. At this point, the radiative lifetime ($\tau_{\text{rad}} = 1/\gamma$) will be introduced in the usual semiempirical manner, giving

$$I(\omega) = \frac{B_1^2}{2\hbar^2} \sum_{c,d} \text{Re} \int_0^{\infty} e^{-i(\omega - \omega_{cd} - i\gamma)\tau} \phi_{cd}(\tau) d\tau.$$

Note that if there were no collisions, then $T = 1$ and ϕ_{cd} is just a constant so that

$$I(\omega) \approx \sum_{c,d} \frac{(\gamma_F B_1)^2}{(1/\tau)^2 + (\omega - \omega_{cd})^2}$$

as is to be expected.

For $\rho(t)$, assuming a steady-state situation, the time dependence of the diagonal terms of the density matrix may be neglected (the off-diagonal terms have already been assumed to be negligible). Hence,

$$\phi_{cd} = \sum_{a,b} \langle a | \bar{\rho}(t) | a \rangle \langle a | \mu_- | b \rangle \langle c | \mu_+ | d \rangle \times \int_{-\infty}^{\infty} \langle b | T^{-1}(t+\tau, t) | c \rangle \langle d | T(t+\tau, t) | a \rangle dt.$$

It will now be shown that in a sense to be defined below, $b = c$ and $d = a$ in order that ϕ_{cd} not vanish. We begin by obtaining a formal expression for $T(t+\tau, t)$ which will display the t dependence of T more clearly. We start with

$$T(t+\tau, t) = \text{“exp”} \left\{ -\frac{i}{\hbar} \int_t^{t+\tau} U_0^{-1}(t', t_0) H_c(t') U_0(t', t_0) dt' \right\},$$

where by “exp” is meant the usual Dyson chronological ordering procedure. It will be clear that the argument which follows does not depend on the distinction between exp and “exp” which in other cases is crucial. We have by a simple identity

$$\begin{aligned} T(t+\tau, t) &= \text{“exp”} \left\{ -\frac{i}{\hbar} \int_t^{t+\tau} U_0^{-1}(t, t_0) U_0(t, t_0) U_0^{-1}(t', t_0) H_c(t') U_0(t', t_0) U_0^{-1}(t, t_0) U_0(t, t_0) dt' \right\} \\ &= \text{“exp”} \left\{ U_0^{-1}(t, t_0) \left(-\frac{i}{\hbar} \right) \int_t^{t+\tau} [U_0(t', t_0) U_0^{-1}(t, t_0)]^{-1} H_c(t') [U_0(t', t_0) U_0^{-1}(t, t_0)] dt' U_0(t, t_0) \right\} \\ &= U_0^{-1}(t, t_0) \text{“exp”} \left\{ -\frac{i}{\hbar} \int_t^{t+\tau} U_0^{-1}(t', t) H_c(t') U_0(t', t) dt' \right\} U_0(t, t_0). \end{aligned}$$

⁸ This is discussed by C. J. Tsao and B. Curnette, Geophysical Research Paper No. 69, September 1960 AFCRL-TR60-278, Department of Commerce, Washington, D. C. (unpublished).

⁹ P. W. Anderson, Phys. Rev. **76**, 647 (1949), hereinafter referred to as Anderson.

Since $U_0(t', t) = \exp[-(i/\hbar)H_0(t' - t)] = U_0(t' - t, 0)$, then upon setting $x = t' - t$,

$$\begin{aligned} T(t + \tau, t) &= U_0^{-1}(t, t_0) \\ &\times \text{"exp"} \left[-\frac{i}{\hbar} \int_0^\tau U_0^{-1}(x, 0) H_c(x + t) \right. \\ &\quad \left. \times U_0(x, 0) dx \right] U_0(t, t_0) \\ &= U_0^{-1}(t, t_0) T_t(\tau) U_0(t, t_0), \end{aligned}$$

where $T_t(\tau)$ is given by

$$T_t(\tau) = \text{"exp"} \left[-\frac{i}{\hbar} \int_0^\tau U_0^{-1}(x, 0) H_c(x + t) U_0(x, 0) dx \right].$$

Hence the expression

$$\int_{-\infty}^{\infty} \langle b | T^{-1}(t + \tau, t) | c \rangle \langle d | T(t + \tau, t) | a \rangle dt$$

becomes

$$\int_{-\infty}^{\infty} e^{i(\omega_{bc} + \omega_{da})t} \langle b | T_t^{-1}(\tau) | c \rangle \langle d | T_t(\tau) | a \rangle dt.$$

It is clear from the assumption of random collisions that $H_c(x)$ is essentially time-translation invariant, and thus $T_t(\tau)$ is essentially independent of t . The t integration thus yields a delta function, $\delta(\omega_{bc} + \omega_{da})$, which means that for a nonzero result we must have $\omega_{bc} + \omega_{da} = 0$ which is equivalent to the original assertion $b = c$ and $d = a$, since to have radiation at all it is necessary that $c \neq d$ and $a \neq b$. In practice, the levels are smeared out by collisions and radiative damping, so that the requirement that levels coincide is expected to be $\omega_{bc} \ll 1/\tau_{\text{eff}}$ and $\omega_{da} \ll 1/\tau_{\text{eff}}$. Since in most work $1/\tau_{\text{eff}}$ is less than one Mc/sec, then as long as the Zeeman splittings are greater than one Mc/sec (they are generally greater than 10 Mc/sec in typical double resonance work) the requirement is just $b = c$ and $d = a$. For very closely spaced levels the situation would be more complicated. Thus ϕ_{cd} reduces to

$$\begin{aligned} \phi_{cd}(\tau) &= \int_{-\infty}^{\infty} \langle d | \bar{\rho}(t) | d \rangle \langle d | \mu_- | c \rangle \langle c | T^{-1}(t + \tau, t) | c \rangle \\ &\quad \times \langle c | \mu_+ | d \rangle \langle d | T(t + \tau, t) | d \rangle dt, \end{aligned}$$

where c and d are adjacent sublevels. Using an obvious notation, our basic formulas in Eq. (5) may be rewritten as

$$I(\omega) = \frac{B_1^2}{2\hbar^2} \sum_{i,f} \text{Re} \int_0^\infty e^{-i(\omega - \omega_{fi} - i\gamma)\tau} \phi_{if}(\tau) d\tau, \quad (6a)$$

$$\begin{aligned} \phi_{if}(\tau) &= \langle i | \bar{\rho}(t) | i \rangle \langle f | \mu_+ | i \rangle^2 \int_{-\infty}^{\infty} \langle f | T^{-1}(t + \tau, t) | f \rangle \\ &\quad \times \langle i | T(t + \tau, t) | i \rangle dt. \quad (6b) \end{aligned}$$

At this point, the rather serious restrictions of the theory should perhaps be emphasized. They are fundamentally two in number: (a) $\gamma_F B_1 \ll 1/\tau_{\text{rad}}$ and (b) the splitting of the magnetic sublevels is large with respect to the width of the lines in question. In the most general magnetic resonance type experiment these two restrictions are not necessarily well obeyed. For example, in the so-called level-crossing experiments¹⁰ the entire effect depends on the fact that the levels are very close to each other, in fact, that they actually intersect. The most general approach to this problem, which brings in the phenomena of light beats,¹¹ level crossing,¹⁰ and coherence narrowing¹² would require a true density matrix formulation of the problem and would be much more difficult to carry through.

Using the methods of Anderson, which we repeat here in simplified form for completeness, it is now a straightforward matter to obtain a simple form for $\phi_{cd}(\tau)$. Calling

$$F(\tau) = \int_{-\infty}^{\infty} \langle f | T^{-1}(t + \tau, t) | f \rangle \langle i | T(t + \tau, t) | i \rangle dt,$$

a differential equation for $F(\tau)$ may now be found.

$$\begin{aligned} dF(\tau) &= \int_{-\infty}^{\infty} [\langle f | T^{-1}(t + \tau + d\tau, t) | f \rangle \langle i | T(t + \tau + d\tau, t) | i \rangle \\ &\quad - \langle f | T^{-1}(t + \tau, t) | f \rangle \langle i | T(t + \tau, t) | i \rangle] dt, \\ dF(\tau) &= \int_{-\infty}^{\infty} [\langle f | T^{-1}(t + \tau, t) T^{-1}(t + \tau + d\tau, t + \tau) | f \rangle \\ &\quad \times \langle i | T(t + \tau + d\tau, t + \tau) T(t + \tau, t) | i \rangle \\ &\quad - \langle f | T^{-1}(t + \tau, t) | f \rangle \langle i | T(t + \tau, t) | i \rangle] dt. \end{aligned}$$

In breaking up the above products into sums over intermediate states, only those terms with intermediate state f (in the first product) and i (in the second product) will contribute by the above arguments. Hence,

$$\begin{aligned} dF(\tau) &= \int_{-\infty}^{\infty} [\langle f | T^{-1}(t + \tau, t) | f \rangle \\ &\quad \times \langle f | T^{-1}(t + \tau + d\tau, t + \tau) | f \rangle \\ &\quad \times \langle i | T(t + \tau + d\tau, t + \tau) | i \rangle \langle i | T(t + \tau, t) | i \rangle \\ &\quad - \langle f | T^{-1}(t + \tau, t) | f \rangle \langle i | T(t + \tau, t) | i \rangle] dt \\ &= - \int_{-\infty}^{\infty} [1 - \langle f | T^{-1}(t + \tau + d\tau, t + \tau) | f \rangle \\ &\quad \times \langle i | T(t + \tau + d\tau, t + \tau) | i \rangle] \\ &\quad \times [\langle f | T(t + \tau, t) | f \rangle \langle i | T(t + \tau, t) | i \rangle] dt. \end{aligned}$$

¹⁰ F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters **3**, 420 (1959); P. A. Franken, Phys. Rev. **121**, 508 (1961); M. E. Rose and R. L. Carovillano, Phys. Rev. **122**, 1185 (1961).

¹¹ J. N. Dodd and G. W. Series, Proc. Roy. Soc. (London) **A263**, 353 (1961).

¹² J. P. Barrat, J. Phys. Radium **20**, 541, 633, 657 (1959).

Now assume that $d\tau$ may be chosen to be much greater than the duration of a collision but also much smaller than the time between collisions. This is the standard "impact" assumption which in this case is obeyed to a very high degree of accuracy (the time between collisions is of the order of 10^{-6} sec and the duration of a collision is of the order of 10^{-11} sec). Then $T(t+\tau, t)$ and $T(t+\tau+d\tau, t+\tau)$ are uncorrelated and the time integration over them may be performed separately. The second term in brackets gives just $F(\tau)$ upon integrating. In the first term, since only one collision occurs in $d\tau$, the time integral may be replaced by an integral over all possible types of collision. Hence,

$$dF(\tau) = -\langle 1 - \langle f | T^{-1}(t+\tau+d\tau, t+\tau) | f \rangle \times \langle i | T(t+\tau+d\tau, t+\tau) | i \rangle \rangle_{\text{av}} F(\tau),$$

where the average is taken over all possible types of collisions. The average over symmetric and antisymmetric states of the two atoms considered as a system can be done simply. Since either of these two states is equally likely,

$$dF(\tau) = -\left\{ 1 - \frac{1}{2} [\langle f | T^{-1}(\rho) | f \rangle_+ \langle i | T(\rho) | i \rangle_+ + \langle f | T^{-1}(\rho) | f \rangle_- \langle i | T(\rho) | i \rangle_-] \right\}_{\text{av}} F(\tau),$$

where the subscripts + and - signify symmetric and antisymmetric states, respectively, and where ρ represents the spacial collision parameters over which the average is taken. Because of the simple significance of symmetric and antisymmetric eigenfunctions this can be written in a simpler form. The interaction considered in this paper will be the dipole-dipole interaction, and hence, if it is of the first-order, resonant type, $\langle |T| \rangle_+ = \langle |T| \rangle_-^*$, i.e., the two matrix elements are connected by simple complex conjugation, whereas for nonresonant interactions $\langle |T| \rangle_+ = \langle |T| \rangle_-$, since the perturbing atom in this case acts like a foreign gas atom. Hence in these two cases

$$dF_1(\tau) = -\text{Re} \langle 1 - \langle f | T^{-1}(\rho) | f \rangle \langle i | T(\rho) | i \rangle \rangle_{\text{av}} F_1(\tau),$$

$$dF_2(\tau) = -\langle 1 - \langle f | T^{-1}(\rho) | f \rangle \langle i | T(\rho) | i \rangle \rangle_{\text{av}} F_2(\tau),$$

where the matrix elements are computed using either symmetric or antisymmetric eigenfunctions.

$$\begin{aligned} I_{m, m+1} &= \frac{1}{2} \langle m | \bar{\rho}(t) | m \rangle \langle m+1 | \mu_+ | m \rangle^2 (\gamma_F B_1)^2 \text{Re} \int_0^\infty \exp(-i\{\omega - \omega_{m+1, m} - i[\gamma + n\bar{v}\sigma(m \rightarrow m+1)]\}\tau) d\tau \\ &= \frac{1}{2} \langle m | \bar{\rho}(t) | m \rangle (F-m)(F+m+1) (\gamma_F B_1)^2 \\ &\quad \times \text{Re} \int_0^\infty \exp\{-i[\omega - \omega_{m+1, m} + n\bar{v}\sigma_I(m \rightarrow m+1)]\tau\} \exp\{-[\gamma + n\bar{v}\sigma_R(m \rightarrow m+1)]\tau\} d\tau, \end{aligned}$$

where by Eq. (7),

$$\sigma(m \rightarrow m+1) = \text{Re} \int [1 - \langle m+1 | T^{-1}(\rho) | m+1 \rangle \langle m | T(\rho) | m \rangle] d\rho,$$

with the omission of Re in the nonresonant case. Now consider the inverse transition, $i=m+1, f=m$. This is the

Now assume that the probability of a collision of type $d\rho$ in $d\tau$ is just $nvd\rho d\tau$, where n is the atomic density, v is the relative velocity of the two particles and $d\rho$ contains a velocity average. Then, with an obvious change for the nonresonant case,

$$\frac{dF(\tau)}{F(\tau)} = -n \left\{ \int v \text{Re} [1 - \langle f | T^{-1}(\rho) | f \rangle \times \langle i | T(\rho) | i \rangle] d\rho \right\} d\tau.$$

Since it is customary to write the collision frequency in the form $n\bar{v}\sigma$, where \bar{v} is the average relative velocity, we will replace v by \bar{v} throughout. This is exact in the resonant case where, as will be shown, σ has a $1/v$ dependence. In general, to be precise, one should actually velocity average the expression for the collision frequency, but since this substitution will involve variations of only a few percent no significant error is made by setting $v=\bar{v}$. Hence $dF(\tau)/F(\tau) = n\bar{v}\sigma d\tau$ and, therefore, $F(\tau) = \exp(-n\bar{v}\sigma\tau)$, where

$$\sigma = \text{Re} \int [1 - \langle f | T^{-1}(\rho) | f \rangle \langle i | T(\rho) | i \rangle] d\rho \quad (7)$$

with the omission of Re in the nonresonant case. Hence

$$\phi_{if} = \langle i | \bar{\rho}(t) | i \rangle \langle f | \mu_+ | i \rangle^2 \exp(-n\bar{v}\sigma\tau),$$

and thus

$$\begin{aligned} I_{if} &= \frac{1}{2} \langle i | \bar{\rho}(t) | i \rangle \langle f | F_+ | i \rangle^2 (\gamma_F B_1)^2 \\ &\quad \times \text{Re} \int_0^\infty \exp\{-i[\omega - \omega_{fi} - i(\gamma + n\bar{v}\sigma)]\tau\} d\tau. \end{aligned}$$

Writing $\sigma = \sigma_R + i\sigma_I$, the signal becomes

$$I_{if} \approx \frac{(\gamma_F B_1)^2}{(\omega - \omega_{fi} + n\bar{v}\sigma_I)^2 + (1/\tau_{\text{rad}} + n\bar{v}\sigma_R)^2}. \quad (8)$$

It is instructive to examine I_{if} more explicitly. Set $f=m+1, i=m$; then for the absorption case described above

emission case, so μ_+ is replaced by μ_- and ω is replaced by $-\omega$. Then

$$I_{m+1,m} = \frac{1}{2} \langle m+1 | \bar{\rho}(t) | m+1 \rangle (F-m)(F+m+1) (\gamma_F B_1)^2 \\ \times \text{Re} \int_0^\infty \exp\{-i[-\omega - \omega_{m,m+1} + n\bar{v}\sigma_I(m+1 \rightarrow m)]\tau\} \exp\{-[\gamma + n\bar{v}\sigma_R(m+1 \rightarrow m)]\tau\} d\tau \\ \sigma(m+1 \rightarrow m) = \text{Re} \int [1 - \langle m | T^{-1}(\rho) | m \rangle \langle m+1 | T(\rho) | m+1 \rangle] d\rho$$

with the omission of Re in the nonresonant case. It is easily seen that $\sigma(m+1 \rightarrow m) = \sigma(m \rightarrow m+1)^*$, so that

$$I_{m+1,m} = \frac{1}{2} \langle m+1 | \bar{\rho}(t) | m+1 \rangle (F-m)(F+m+1) (\gamma_F B_1)^2 \\ \times \text{Re} \int_0^\infty \exp\{+i[\omega - \omega_{m+1,m} + n\bar{v}\sigma_I(m \rightarrow m+1)]\tau\} \exp\{-[\gamma + n\bar{v}\sigma_R(m \rightarrow m+1)]\tau\} d\tau.$$

Thus, $I_{m,m+1}$ and $I_{m+1,m}$ are the same except for the multiplicative factors of $\langle m | \bar{\rho}(t) | m \rangle$ and $\langle m+1 | \bar{\rho}(t) | m+1 \rangle$. They are broadened by the same amount and shifted in the same direction by equal amounts, as we must require on physical grounds. In an experiment, the difference between $I_{m,m+1}$ and $I_{m+1,m}$ is the observed quantity, and thus the observed signal is proportional to the difference between the populations of the two levels in question, as should be expected. In a similar manner it may readily be checked that the transition $-m \rightarrow -(m+1)$ in the emission case gives the same magnitude of signal (provided the levels m and $-m$ have equal population) and the same broadening as in the absorption case $m \rightarrow m+1$, but the line is shifted by $-n\bar{v}\sigma_I/2\pi$ cps in the former case as opposed to $+n\bar{v}\sigma_I/2\pi$ in the latter case. In both cases the half-width (full width at half-maximum intensity) is

$$\Delta_{1/2} = \frac{1}{\pi\tau_{\text{rad}}} + \frac{n\bar{v}\sigma_R}{\pi} \quad (\text{in cps}).$$

Thus in the case of the first-order resonant interaction the line will be broadened, but there will be no shift of line center since the cross section σ has no imaginary part. We may point out here that in the double resonance case, where transitions take place between magnetic sublevels, it is clear that although an individual collision will cause a shift, this should always vanish when averaged over all collision directions. This will be shown explicitly in Sec. III.

The final part of the formal solution is to find a method of evaluating matrix elements of the form $\langle n | T(\rho) | n \rangle$. Recall the equation for T ,

$$i\hbar\dot{T} = [U_0^{-1}(t,t_0)H_c^\rho(t)U_0(t,t_0)]T,$$

where $H_c^\rho(t)$ is now the Hamiltonian for a single collision parametrized by ρ . Since, in general, $U_0^{-1}(t,t_0) \times H_c^\rho(t)U_0(t,t_0)$ does not commute with itself at different times, the integration of the above equation will involve complicated time-ordered products of terms which, in general, are quite untractable. However, in this case the physics of our special situation enables us

to evaluate T in closed form. Taking matrix elements on both sides of the above equation, we get, using the summation convention on primed indices,

$$i\hbar\langle n | \dot{T} | n \rangle = \langle n | U_0^{-1}(t,t_0) | n' \rangle \langle n' | H_c^\rho(t) | n'' \rangle \\ \times \langle n'' | U_0(t,t_0) | n''' \rangle \langle n''' | T | n \rangle \\ = e^{i\omega_{nn'}t} \langle n | H_c^\rho(t) | n' \rangle \langle n' | T | n \rangle,$$

where $\omega_{nn'} = (E_n - E_{n'})/\hbar$. Two limiting cases arise. First, if the duration δt of the collision is long with respect to all the $\omega_{nn'}$ involved, then the rapid oscillation of $e^{i\omega_{nn'}t}$ will give zero unless $\omega_{nn'} = 0$, i.e., unless $n = n'$. Then

$$i\hbar\langle n | \dot{T} | n \rangle = \langle n | H_c^\rho(t) | n \rangle \langle n | T | n \rangle,$$

$$\langle n | T | n \rangle = \exp\left[-(i/\hbar) \int_{t_0}^t \langle n | H_c^\rho(t') | n \rangle dt'\right].$$

Thus

$$\langle n | T(\rho) | n \rangle = \exp\left[-(i/\hbar) \int_{-\infty}^{\infty} \langle n | H_c^\rho(t) | n \rangle dt\right],$$

where the t in $H_c^\rho(t)$ arises from the classical trajectory assumption. This is just the well-known phase-shift result.¹³ The other limit of interest is our case, namely, if δt is much less than the periods involved in our problem which are, as mentioned before, $T = 10^{-7}$ to 10^{-8} sec. Since δt is of order b/\bar{v} , where b is the distance of closest approach, $b \lesssim 10^{-6}$ cm, and $\bar{v} \approx 10^5$ cm/sec, we see that δt is a factor of 10^{-3} to 10^{-4} smaller than T . Thus the oscillatory factors may be considered equal to unity during a collision, and

$$T = \exp\left[-(i/\hbar) \int_{-\infty}^{\infty} H_c^\rho(t) dt\right], \quad (9)$$

where $H_c^\rho(t)$ is to be thought of as a matrix involving the magnetic sublevels in question, i.e., a $(2F+1) \times (2F+1)$ matrix.

Although this gives a formal solution to the problem,

¹³ H. M. Foley, Phys. Rev. **69**, 616 (1946).

for the purposes of calculation some further manipulation is desirable. Consider the collision as shown in Fig. 1, where the coordinate system is chosen so that the z axis lies along the distance of closest approach b . Since a magnetic field is present, the matrix $H_c^\rho(t)$ will have an angular dependence. Note, however, that it is a simple matter to calculate $H_c^\rho(t)$ in the special case that \mathbf{B}_0 lies along b . The $(2F+1)$ -rowed representation of the rotation group can then be used to rotate the field to (θ, ϕ) . Let us call $M(\rho) = \int_{-\infty}^{\infty} H_c^\rho(t) dt$, where \mathbf{B}_0 is taken along b . Then $T(\rho)$ becomes

$$T(\rho) = \exp\left[-\frac{i}{\hbar} D^{(F)-1}(\theta, \phi) M(\rho) D^F(\theta, \phi)\right],$$

where $D^F(\theta, \phi)$ is the $(2F+1)$ -rowed representation of the rotation group. Now $M(\rho)$ will be Hermitian. Let S be the unitary matrix which diagonalizes $M(\rho)$. The calculation of this matrix is greatly simplified by the fact that the parameters b and \bar{v} come out of $M(\rho)$ in a common factor. Thus, $M(\rho)$ is just an array of numbers.

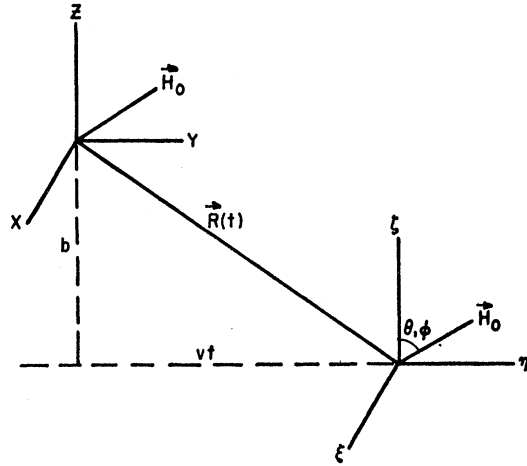


FIG. 1. The coordinate system for a collision between two atoms.

It is easy to see that if S diagonalizes $M(\rho)$, i.e., if $[S^{-1}M(\rho)S]_{ij} = \mu_i \delta_{ij}$, then $D^{(F)-1}(\theta, \phi)S$ diagonalizes $D^{(F)-1}(\theta, \phi)M(\rho)D^F(\theta, \phi)$. Hence

$$T(\rho) = D^{(F)-1}(\theta, \phi)S \exp\left[-\frac{i}{\hbar} \begin{bmatrix} \mu_1(\rho) & 0 & \dots & 0 \\ 0 & \mu_2(\rho) & & \vdots \\ \vdots & & \ddots & \vdots \\ 0 & \dots & \dots & \mu_{2F+1}(\rho) \end{bmatrix}\right] [D^{(F)-1}(\theta, \phi)S]^{-1}.$$

Since the exponential of a diagonal matrix is equal to a diagonal matrix of the exponentials, we get finally

$$T(\rho) = [D^{(F)-1}(\theta, \phi)S] \begin{bmatrix} e^{-i\mu_1(\rho)/\hbar} & 0 & \dots & 0 \\ 0 & e^{-i\mu_2(\rho)/\hbar} & & \vdots \\ \vdots & & \ddots & \vdots \\ 0 & \dots & \dots & e^{-i\mu_{2F+1}(\rho)/\hbar} \end{bmatrix} [D^{(F)-1}(\theta, \phi)S]^{-1}.$$

From this expression, it is a simple matter to obtain any desired matrix element of $T(\rho)$. One now forms

$$[1 - \langle f | T^{-1}(\rho) | f \rangle \langle i | T(\rho) | i \rangle]$$

averages over all possible orientations of the magnetic field and then integrates over $2\pi b db$ to obtain the cross section.

It is clear that the $\mu_i(\rho)$ must bear some analogy to the phase shifts of the usual, adiabatic theory.¹³ For the relevant matrix elements, expressions of the form

$$\begin{aligned} \langle f | T^{-1}(\rho) | f \rangle &= \sum_j f_j e^{i\mu_j(\rho)/\hbar} \\ \langle i | T(\rho) | i \rangle &= \sum_{j'} g_{j'} e^{-i\mu_{j'}(\rho)/\hbar} \end{aligned}$$

will be obtained, and hence,

$$\begin{aligned} \langle f | T^{-1}(\rho) | f \rangle \langle i | T(\rho) | i \rangle \\ = \sum_{j, j'} f_j g_{j'} \exp\left\{\frac{i}{\hbar} [\mu_j(\rho) - \mu_{j'}(\rho)]\right\}. \end{aligned}$$

The quantities $(\mu_j - \mu_{j'})$ are the analogs of the phase shifts in the adiabatic theory, although they are not simply time averages of the difference in collision energies between states j and j' , but contain the effects of transitions in their structure.

III. SPECIFIC EXAMPLES

The dipole-dipole interaction will be taken as the collision Hamiltonian. Upon expanding the electrostatic potential between two electrically neutral atoms, this is found to be

$$H_c(t) = \frac{1}{R^3(t)} \left\{ 3 \frac{[\mathbf{p} \cdot \mathbf{R}(t)][\boldsymbol{\pi} \cdot \mathbf{R}(t)]}{R^2} - \mathbf{p} \cdot \boldsymbol{\pi} \right\}, \quad (10)$$

where Latin letters refer to one atom, Greek letters to the other, and $\mathbf{p} = e\sum_i \mathbf{r}_i$, \mathbf{r}_i being the radius vector from the nucleus of one atom to its i th electron. $\mathbf{R}(t)$ is the internuclear vector between the two atoms, depending on time via the classical trajectory assumption (the

trajectory has been taken to be a straight line, an approximation which can readily be seen to involve only a very small error). In keeping with the assumptions of Sec. II, atomic frequencies are neglected. Using the coordinate system of Fig. 1, $H_c(t)$ may be expanded to give

$$H_c(t) = A \frac{b^2}{R^5(t)} + B \frac{b\bar{v}t}{R^5(t)} + C \frac{1}{R^3(t)},$$

$$R(t) = (b^2 + \bar{v}^2 t^2)^{1/2},$$

where

$$A = 3(p_z\pi_\zeta - p_y\pi_\eta), \quad B = -3(p_z\pi_\zeta + p_y\pi_\eta),$$

$$C = (2p_y\pi_\eta - p_x\pi_\xi - p_z\pi_\zeta).$$

Now, the expression

$$T = \exp \left[-\frac{i}{\hbar} \int_{-\infty}^{\infty} H_c(t) dt \right]$$

must be evaluated. The three time integrations are trivial. The first gives $4/(3b^2\bar{v})$, the second vanishes by symmetry and the third gives $2/(b^2\bar{v})$. Hence

$$T = \exp \left[-\frac{4i}{\hbar b^2\bar{v}} \left(\frac{1}{3}A + \frac{1}{2}C \right) \right] = \exp \left[-\frac{2i}{\hbar b^2\bar{v}} (p_z\pi_\zeta - p_x\pi_\xi) \right].$$

An examination of the original expression for $H_c(t)$ shows that the term $(p_z\pi_\zeta - p_x\pi_\xi)$ is what we would expect if the interaction were considered to be a delta function in time, normalized in an appropriate way. Then $\mathbf{R}(t) \rightarrow \mathbf{z}$, and the x and y axes are equivalent, giving the result above. This is essentially the meaning of the assumption that, in solving the original equation for T , terms which do not commute with each other at different times may be neglected.

The matrix T must now be evaluated using eigenfunctions symmetric (or antisymmetric) in the two atoms. Thus we want

$$M_1^{mm'} = \frac{1}{2} \langle \phi_a^0(\mathbf{r}) \phi_e^m(\boldsymbol{\rho}) + \phi_e^m(\mathbf{r}) \phi_a^0(\boldsymbol{\rho}) | p_z\pi_\zeta - p_x\pi_\xi | \phi_a^0(\mathbf{r}) \phi_e^{m'}(\boldsymbol{\rho}) + \phi_e^{m'}(\mathbf{r}) \phi_a^0(\boldsymbol{\rho}) \rangle,$$

where ϕ_a is taken to be a 1S_0 state and ϕ_e to be any state with $J=1$ (in practice, ϕ_e will usually be the lowest 3P_1 state). This reduces to

$$M_1^{mm'} = \langle \phi_a^0(\mathbf{r}) | p_z | \phi_e^{m'}(\mathbf{r}) \rangle \langle \phi_e^m(\boldsymbol{\rho}) | \pi_\zeta | \phi_a^0(\boldsymbol{\rho}) \rangle - \langle \phi_a^0(\mathbf{r}) | p_x | \phi_e^{m'}(\mathbf{r}) \rangle \langle \phi_e^m(\boldsymbol{\rho}) | \pi_\xi | \phi_a^0(\boldsymbol{\rho}) \rangle.$$

Evaluating this in terms of reduced matrix elements,¹⁴

$$M_1^{mm'} = |\langle g || \mathbf{p} || e \rangle|^2 \begin{bmatrix} -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{bmatrix},$$

where m and m' values decrease from the upper left corner. Hence

$$T = \exp \left\{ -\frac{2i}{\hbar b^2\bar{v}} |\langle g || \mathbf{p} || e \rangle|^2 \begin{bmatrix} -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{bmatrix} \right\}.$$

It is obvious that any matrix of the form

$$\begin{bmatrix} a & 0 & c \\ 0 & b & 0 \\ c & 0 & a \end{bmatrix}$$

can be diagonalized by a matrix U given by

$$\begin{bmatrix} \lambda_0 & 0 & 0 \\ 0 & \lambda_+ & 0 \\ 0 & 0 & \lambda_- \end{bmatrix} = \begin{bmatrix} 0 & 2^{-1/2} & 2^{-1/2} \\ 1 & 0 & 0 \\ 0 & 2^{-1/2} & -2^{-1/2} \end{bmatrix}^{-1} \begin{bmatrix} a & 0 & c \\ 0 & b & 0 \\ c & 0 & a \end{bmatrix} \begin{bmatrix} 0 & 2^{-1/2} & 2^{-1/2} \\ 1 & 0 & 0 \\ 0 & 2^{-1/2} & -2^{-1/2} \end{bmatrix}, \quad (11)$$

where $\lambda_0 = b$, $\lambda_+ = a + c$, $\lambda_- = a - c$.

At this point we calculate the collision cross section for a general interaction matrix, M , of this form, since this type will again occur later. Since $J=1$, the three-rowed representation of the rotation group is relevant. It is given by¹⁵

$$D^{(1)} = \begin{bmatrix} \frac{1}{2}(1 + \cos\beta)e^{i(\alpha+\gamma)} & 2^{-1/2}\sin\beta e^{i\alpha} & \frac{1}{2}(1 - \cos\beta)e^{i(\alpha-\gamma)} \\ -2^{-1/2}\sin\beta e^{i\gamma} & \cos\beta & 2^{-1/2}\sin\beta e^{-i\gamma} \\ \frac{1}{2}(1 - \cos\beta)e^{-i(\alpha-\gamma)} & -2^{-1/2}\sin\beta e^{-i\alpha} & \frac{1}{2}(1 + \cos\beta)e^{-i(\alpha+\gamma)} \end{bmatrix},$$

where (α, β, γ) are the usual three Euler angles. Using this matrix, T becomes

$$T = [D^{(1)-1}U] \begin{bmatrix} e^{ib} & 0 & 0 \\ 0 & e^{i(a+c)} & 0 \\ 0 & 0 & e^{i(a-c)} \end{bmatrix} [D^{(1)-1}U]^{-1}. \quad (12)$$

¹⁴ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957).

¹⁵ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

Performing the necessary multiplication it is a simple matter to find the diagonal elements of T ,

$$\begin{aligned}\langle 1|T|1\rangle &= \frac{1}{2}[\sin^2\beta e^{ib} + (\cos^2\alpha + \cos^2\beta \sin^2\alpha)e^{i(\alpha+c)} + (\sin^2\alpha + \cos^2\beta \sin^2\alpha)e^{i(\alpha-c)}], \\ \langle 0|T|0\rangle &= \cos^2\beta e^{ib} + \sin^2\beta \sin^2\alpha e^{i(\alpha+c)} + \sin^2\beta \cos^2\alpha e^{i(\alpha-c)}, \\ \langle -1|T|-1\rangle &= \langle 1|T|1\rangle.\end{aligned}$$

As we should expect, there is complete symmetry between $m=1$ and $m=-1$, and hence the result for broadening of the transition $m=1 \rightarrow m=0$ will be identical with that for $m=-1 \rightarrow m=0$. We consider only the former, obtaining

$$\begin{aligned}\sigma &= \int [1 - \langle 0|T^{-1}|0\rangle \langle 1|T|1\rangle] d\rho, \\ \text{Re}\sigma &= \int \left\{ 1 - \frac{1}{2}[\sin^2\beta \cos^2\beta + 2 \sin^2\beta \sin^2\alpha \cos^2\alpha + \sin^2\beta \cos^2\beta (\sin^4\alpha + \cos^4\alpha)] \right. \\ &\quad \left. - \frac{1}{2}[\cos^2\beta \cos^2\alpha + (\cos^4\beta + \sin^4\beta) \sin^2\alpha] \cos(a-b+c) - \frac{1}{2}[\cos^2\beta \sin^2\alpha + (\cos^4\beta + \sin^4\beta) \cos^2\alpha] \cos(a-b-c) \right. \\ &\quad \left. - \frac{1}{2}[\sin^2\beta (\sin^4\alpha + \cos^4\alpha) + 2 \sin^2\beta \cos^2\beta \sin^2\alpha \cos^2\alpha] \cos 2c \right\} d\rho, \\ \text{Im}\sigma &= \frac{1}{2} \int \left\{ [\cos^2\beta - \sin^2\beta \sin^2\alpha] \sin(a-b+c) + [\cos^2\beta - \sin^2\beta \cos^2\alpha] \sin(a-b-c) + \sin^2\beta (\cos^2\alpha - \sin^2\alpha) \sin 2c \right\} d\rho.\end{aligned}$$

Now we must average over Euler angles, i.e., integrate over $\sin\beta d\beta d\alpha d\gamma/8\pi^2$. If we do this, it is easy to see that $\text{Im}\sigma=0$, as asserted above. For the real part of σ , we find after averaging

$$\text{Re}\sigma = \sigma = \frac{16\pi}{15} \int_0^\infty [\sin^2\frac{1}{2}(a-b'+c) + \sin^2\frac{1}{2}(a-b'-c) + \sin^2c] b db.$$

In the resonant case which we are considering, $a=\alpha/b^2$, $b'=-2\alpha/b^2$ and $c=-\alpha/b^2$, where $\alpha=g|\langle \mathbf{p}|e\rangle|^2/\hbar\bar{\nu}$. Thus, using Eq. (12), we get

$$\sigma = \frac{16\pi}{15} \int_0^\infty \left[\sin^2\frac{2\alpha}{b^2} + 2 \sin^2\frac{\alpha}{b^2} \right] b db.$$

The indicated integrations are readily performed to yield

$$\sigma = \frac{16\pi^2}{15} \frac{|\langle \alpha|\mathbf{p}|e\rangle|^2}{\hbar\bar{\nu}}.$$

Using the familiar result,¹⁴ $32\pi^3 |\langle g|\mathbf{p}|e\rangle|^2/3\hbar\lambda^3 = 1/\tau$, where λ is the wavelength corresponding to the transition from the excited state to the ground state, and τ is the lifetime of the excited state, the cross section becomes

$$\sigma = \frac{1}{10\pi} \frac{\lambda^3/\tau}{\bar{\nu}}, \quad (13a)$$

or in terms of the oscillator strength f of the transition in question

$$\sigma = \frac{4\pi r_0 c \lambda f}{15 \bar{\nu}}. \quad (13b)$$

r_0 is the classical electron radius. Values of σ , along with the relevant constants are given for some cases of interest in Table I.

Table I shows that the cross section for resonant broadening decreases very sharply in going from heavy atoms to light atoms as the assumption of Russell-Saunders coupling gets better and better, increasing the forbiddenness of the singlet-triplet transition which is the main broadening mechanism. However, in practice such a sharp reduction is not found.^{1,2} The experimental cross sections in zinc and cadmium differ by less than a factor of two, and both are larger than the theoretical cross section for cadmium. The reason for this may be seen by considering the fact that as the oscillator

TABLE I. Self-broadening cross sections for the lowest 3P_1 state of the group II metals.

Atom	Lifetime of state	Wavelength	σ_1^d	σ_2^e	σ_{th}^f	σ_{exp}
Mercury	1.18×10^{-7} sec ^a	2537 Å	1.7×10^{-18} cm ²	4.2×10^{-14} cm ²	1.7×10^{-18} cm ²	$10^{-18} - 10^{-12}$ cm ²
Cadmium	2.39×10^{-6} sec ^b	3261 Å	1.0×10^{-14} cm ²	2.3×10^{-14} cm ²	2.3×10^{-14} cm ²	2.5×10^{-14} cm ²
Zinc	3.2×10^{-5} sec ^c	3076 Å	4.7×10^{-16} cm ²	1.4×10^{-14} cm ²	1.4×10^{-14} cm ²	1.4×10^{-14} cm ²

^a See Ref. 12 for the measurement of the lifetime of the lowest 3P_1 state and the self-broadening in this state.

^b See Ref. 2 for the measurement of the lifetime of the lowest 3P_1 state and the self-broadening in this state.

^c See Ref. 1 for the measurement of the lifetime of the lowest 3P_1 state and the self-broadening in this state.

^d σ_1 is the resonant cross section [Eq. (13a)].

^e σ_2 is the cross section calculated by assuming that the broadening occurs via intermediate states [Eq. (16)].

^f σ_{th} is the larger of σ_1 and σ_2 .

strength of the singlet-triplet transition gets smaller and smaller it is possible for second-order terms in the perturbation evaluation of $\langle m|H_c(t)|m' \rangle$ to become larger than the first-order terms because of the peculiar nature of the resonance interaction which operates in first order.

In writing down the second-order sum over inter-

mediate states, intercombination terms, which will have a negligible effect in cases of interest, will be neglected. Thus, the perturber acts like a foreign gas atom, and the use of symmetric or antisymmetric two-particle wave functions is unnecessary; simple product wave functions of the form $\phi_a(\mathbf{r})\phi_b(\boldsymbol{\rho})$ will be sufficient. The desired expression is

$$M_2^{mm'} = \frac{a_0^4}{R^6} \sum_{e', e''} [\langle \phi_{\sigma}(\mathbf{r})\phi_{e^m}(\boldsymbol{\rho}) | 3(\mathbf{p} \cdot \mathbf{n})(\boldsymbol{\pi} \cdot \mathbf{n}) - \mathbf{p} \cdot \boldsymbol{\pi} | \phi_{e'}(\mathbf{r})\phi_{e''}(\boldsymbol{\rho}) \rangle \times \langle \phi_{e'}(\mathbf{r})\phi_{e''}(\boldsymbol{\rho}) | 3(\mathbf{p} \cdot \mathbf{n})(\boldsymbol{\pi} \cdot \mathbf{n}) - \mathbf{p} \cdot \boldsymbol{\pi} | \phi_{\sigma}(\mathbf{r})\phi_{e^{m'}}(\boldsymbol{\rho}) \rangle (E_{e'} + E_{e''} - E_e - E_{\sigma})^{-1}],$$

where the e' sum is over the singlet series and the e'' sum is over the triplet series. \mathbf{n} is the unit vector along the line connecting the two atomic nuclei, and \mathbf{r} and $\boldsymbol{\rho}$ are measured in units of the Bohr radius a_0 for future convenience in evaluating radial integrals with Slater wave functions.¹⁶

It is clearly impossible to carry out the above sum exactly. However, in cases of interest, such as zinc and cadmium, the arrangement of energy levels is such as to enable to replace $(E_{e'} + E_{e''} - E_e - E_{\sigma})$ by an average value. The lowest energy levels for cadmium and zinc are shown in Figs. 2 and 3, respectively. As far as the singlet series is concerned, the dominant term will be $^1S_0 \rightarrow ^1P_1$; this transition has an oscillator strength of about 1.5 for both zinc and cadmium.¹⁷ Since the sum of all the oscillator strengths for transitions from the 1S_0 level is expected to be about two, it is clear that the other levels contribute very little to our series. We have estimated on the basis of Figs. 2 and 3 that $\langle E_{e'} - E_{\sigma} \rangle_{av}$ for the singlet series will be about 50 000 cm^{-1} . For the triplet series, the work of Ornstein *et al.*¹⁸ has shown that almost all of the oscillator strength sum from transitions from the 3P_1 level comes from the cluster of

levels shown in the triplet part of Figs. 2 and 3. We have estimated $\langle E_{e''} - E_{\sigma} \rangle_{av} = 30\,000\text{ cm}^{-1}$. Thus we will replace our energy denominators with $\langle \Delta E \rangle_{av} = 80\,000\text{ cm}^{-1}$, i.e., 1.6×10^{-11} ergs. The sum over intermediate states is now trivial, giving

$$M_2^{mm'} = \frac{a_0^4}{\langle \Delta E \rangle_{av} R^6} \langle \phi_{\sigma}(\mathbf{r})\phi_{e^m}(\boldsymbol{\rho}) | \times [3(\mathbf{p} \cdot \mathbf{n})(\boldsymbol{\pi} \cdot \mathbf{n}) - \mathbf{p} \cdot \boldsymbol{\pi}]^2 | \phi_{\sigma}(\mathbf{r})\phi_{e^{m'}}(\boldsymbol{\rho}) \rangle$$

and thus,

$$T = \exp \left\{ -\frac{i}{\hbar} \int_{-\infty}^{\infty} \frac{a_0^4}{\langle \Delta E \rangle_{av} R^6} \langle \phi_{\sigma}(\mathbf{r})\phi_{e^m}(\boldsymbol{\rho}) | \times [3(\mathbf{p} \cdot \mathbf{n})(\boldsymbol{\pi} \cdot \mathbf{n}) - \mathbf{p} \cdot \boldsymbol{\pi}]^2 | \phi_{\sigma}(\mathbf{r})\phi_{e^{m'}}(\boldsymbol{\rho}) \rangle dt \right\}.$$

The evaluation of the matrix elements as well as the time integrations is straightforward but rather tedious. The radial integrals will clearly be average values of r^2 for a $5s$ or $5p$ electron in the case of cadmium or a $4s$ or $4p$ electron in the case of zinc. Slater radial wave functions¹⁶ are expected to be most accurate just for such integrals, since their lack of nodes is much less serious than in the case of computing matrix elements between different states, where interference effects may be important. For both s and p electrons in cadmium (and similarly in zinc), Slater's n^* and Z^* are the same. A lengthy calculation gives

$$T = \exp \left\{ -\frac{i\pi e^4 a_0^4}{480 \langle \Delta E \rangle_{av} \hbar v b^5} \times \left[\frac{n^{*2}(n^* + \frac{1}{2})(n^* + 1)}{Z^{*2}} \right]^2 \begin{bmatrix} 498 & 0 & -6 \\ 0 & 444 & 0 \\ -6 & 0 & 498 \end{bmatrix} \right\}.$$

In writing this down, the contribution from the first order is assumed to be so small that it may be neglected with respect to the second order. It should be emphasized that one must not calculate a "first-order cross section" and a "second-order cross section" and

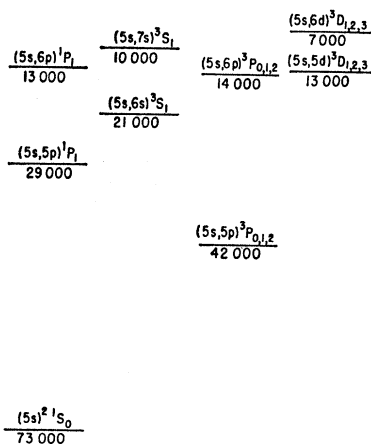


FIG. 2. Relevant energy levels of cadmium (in wave numbers).

¹⁶ J. C. Slater, Phys. Rev. **36**, 57 (1930).

¹⁷ A. Lurio and A. Landman (private communication).

¹⁸ L. S. Ornstein, J. P. A. van Hengstum, and H. Brinkman, Physica **5**, 145 (1938); J. W. Schuttevaer and J. A. Smit, *ibid.* **10**, 502 (1943); see also D. R. Bates and A. Damgaard, Phil. Trans. Proc. Roy. Soc. London **A242**, 101 (1950).

then add the two. To be precise, one should write

$$T = \exp \left[-\frac{i}{\hbar} (M_1 + M_2) \right].$$

Since M_1 and M_2 commute

$$T = e^{-(i/\hbar)M_1} e^{-(i/\hbar)M_2},$$

and because they may be diagonalized simultaneously

$$T = (D^{(1)-1}U) e^{-(i/\hbar)D_1} e^{-(i/\hbar)D_2} (D^{(1)-1}U)^{-1},$$

where D_1 and D_2 are diagonal matrices corresponding to M_1 and M_2 .

Thus the expression for the cross section may readily be formed, taking some care in this case to average properly over symmetric and antisymmetric collision states. However, the eventual integration over all distances of closest approach b is quite complicated and must be done numerically. One such example has been done. For cadmium, where the "first-order cross section" is 1.0×10^{-14} cm² and the "second-order cross section" is 2.3×10^{-14} cm² (neglecting intercombination matrix elements) under typical double resonance operating conditions, the total cross section is only 2.4×10^{-14} cm². Thus it appears that, given the approximation already made, it is sensible to include only the dominant term in the exponential except in an anomalous case where the two terms are very nearly equal. The reason for this effect is that the cross section is essentially determined by an "effective collision radius" at which the collisions reach a strength such that the probability of causing a transition is about 50%. Given the rapidly varying nature of the forces (A/R^3 or B/R^6), this radius may be expected to be determined in most cases by one term or the other. Inside this radius, no matter how strong the collisions, the probability referred to above will vary in an oscillatory manner about 50%. Thus, although for r sufficiently large, the A/R^3 term must eventually dominate, the term in B/R^6 may determine the "effective collision radius" and hence the entire effect.

Now, setting

$$\beta = \frac{\pi e^4 a_0^4}{480 \langle \Delta E \rangle_{\text{av}} \hbar \bar{v}} \left[\frac{n^{*2} (n^* + \frac{1}{2}) (n^* + 1)}{Z^{*2}} \right]^2$$

we note that our T matrix is of the type discussed in obtaining Eq. (12), if we call $a = -498\beta/b^5$, $b' = -444\beta/b^5$, and $c = 6\beta/b^5$. Thus,

$$\sigma = \frac{16\pi}{15} \int_0^\infty \left[\sin^2 \frac{30\beta}{b^5} + \sin^2 \frac{24\beta}{b^5} + \sin^2 \frac{6\beta}{b^5} \right] b db.$$

Making use of the relation

$$\int_0^\infty \sin^2 \frac{A}{b^p} b db = \frac{\pi \csc \pi/p}{8 \Gamma(2/p)} (2A)^{2/p} (p > 1), \quad (14)$$

which may be derived by partial integration followed by contour integration, we get

$$\sigma = \frac{4}{15} \left[(12)^{2/5} + (48)^{2/5} + (60)^{2/5} \right] \frac{\pi^2 \csc \pi/5}{5 \Gamma(7/5)} \beta^{2/5}. \quad (15)$$

If our above result for σ_R is rewritten, the cross section for collision broadening in the second-order case is given by

$$\sigma_R = 1.70 \left\{ \frac{e^4 a_0^4}{\langle \Delta E \rangle_{\text{av}} \hbar \bar{v}} \left[\frac{n^{*2} (n^* + 1/2) (n^* + 1)}{Z^{*2}} \right]^2 \right\}^{2/5}. \quad (16)$$

For cadmium, $n^* = 4$, $Z^* = 4.35$, and $\langle \Delta E \rangle_{\text{av}} = 1.6 \times 10^{-11}$ ergs, so

$$\sigma_R(\text{Cd}) = \frac{1.7 \times 10^{-12}}{\bar{v}^{2/5}} \text{ cm}^2 \\ (= 2.3 \times 10^{-14} \text{ cm}^2 \text{ for } T = 550^\circ \text{K}),$$

and for zinc, $n^* = 3.7$, $Z^* = 4.35$, and $\langle \Delta E \rangle_{\text{av}} = 1.6 \times 10^{-11}$ ergs, so

$$\sigma_R(\text{Zn}) = \frac{1.2 \times 10^{-12}}{\bar{v}^{2/5}} \text{ cm}^2 \\ (= 1.4 \times 10^{-14} \text{ cm}^2 \text{ for } T = 575^\circ \text{K}).$$

On the basis of the approximations made, we feel that these results are accurate to about 15%.

The increase of the width of double resonance lines with temperature in the 3P_1 state of cadmium has been

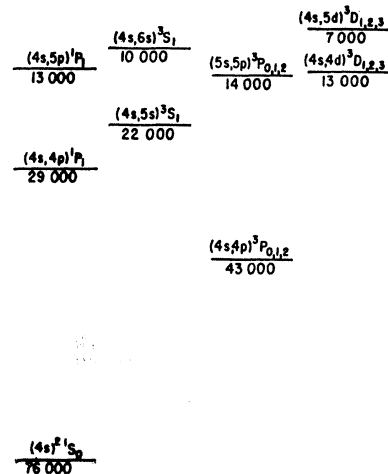


FIG. 3. Relevant energy levels of zinc (in wave numbers).

TABLE II. Foreign-gas broadening cross sections for the lowest 3P_1 state of mercury.

Colliding atom	$n^*_{\text{coll}}^a$	$Z^*_{\text{coll}}^a$	$\langle \Delta E \rangle_{\text{av}}$ in ergs ^b	$\sigma_{\text{th}}(4.2)^c$	$\sigma_{\text{th}}(4.3)^c$	σ_{exp}^d
Helium	1.0	1.70	4.55×10^{-11}	33 ± 5	34 ± 5	38 ± 6
Neon	2.0	5.85	3.96×10^{-11}	42 ± 7	44 ± 7	41 ± 6
Argon	3.0	6.75	3.17×10^{-11}	86 ± 14	88 ± 15	91 ± 14
Krypton	3.7	8.25	2.77×10^{-11}	118 ± 20	122 ± 20	180 ± 27
Xenon	4.0	8.25	2.57×10^{-11}	144 ± 24	150 ± 25	189 ± 29

^a n^*_{coll} and Z^*_{coll} are Slater's principle quantum number and effective charge for the noble gas in question.

^b $\langle \Delta E \rangle_{\text{av}}$ is the mean excitation energy, defined in the text, used to evaluate second-order perturbation theory sums over intermediate states.

^c The two values of σ_{th} (in Å²) are calculated from the expression derived in the text [Eq. (17)] using $n^*_{\text{Hg}}=4.2$ and $n^*_{\text{Hg}}=4.3$.

^d σ_{exp} is the experimental cross section as measured by Piketty-Rives.

observed,² and the cross section has been found to be

$$\sigma = \frac{1.9 \times 10^{-12}}{\bar{v}^{2/5}} \text{ cm}^2 \quad (\text{=} 2.5 \times 10^{-14} \text{ cm}^2 \text{ for } T = 550^\circ \text{K}).$$

Similar measurements have been made by Dumont¹ on the first 3P_1 state in zinc. He finds a mean cross section in the temperature range near 300°C of $\sigma_R = 1.4 \times 10^{-14}$ cm² on what appears to be his most reliable set of data. Since the experimental and theoretical results are accurate to about 15%, the agreement between theory and experiment is quite satisfactory. These results are all summarized in Table I.

It is a simple matter to extend our above result to the case of broadening by a foreign gas atom:

$$\sigma = 1.70 \left\{ \frac{e^4 a_0^4}{\langle \Delta E \rangle_{\text{av}} \hbar \bar{v}_{12}} \left[\frac{n^*(n^*+1/2)(n^*+1)}{Z^{*2}} \right]_{\text{coll}} \times \left[\frac{n^{*2}(n^*+1/2)(n^*+1)}{Z^{*2}} \right]^{2/5} \right\}, \quad (17)$$

where the subscript "coll" refers to the colliding foreign gas atom which causes the broadening, \bar{v}_{12} is the average relative velocity of atom being studied in double resonance and the perturbing atom, and $\langle \Delta E \rangle_{\text{av}}$ is an average excitation energy which must be estimated in the manner indicated above for cadmium-cadmium collisions and zinc-zinc collisions. For noble gas atoms in the 1S_0 ground state, the estimation of $\langle \Delta E \rangle_{\text{av}}$ is facilitated by the fact that all the attainable singlet states cluster around the ionization limit, and transitions to the triplet states are forbidden. Foreign gas broadening of double resonance lines in mercury has been observed by Piketty-Rives.³ Table II gives the various parameters for the mercury-noble-gas systems, along with the theoretical cross sections for $n^*_{\text{Hg}}=4.2$ and $n^*_{\text{Hg}}=4.3$ (in all cases, $Z^*_{\text{Hg}}=4.35$ as in cadmium and zinc). Slater lists $n^*=4.2$ for mercury,¹⁶ but the definition of n^* is probably not good enough to sustain a distinction between $n^*=4.2$ and $n^*=4.3$. Table II

shows that the agreement with the results of Piketty-Rives is quite satisfactory.

As a final application of our method, we may point out that the sudden approximation may be combined with the adiabatic approximation to calculate the cross section for resonance broadening in the usual optical case, in which a transition is being broadened in either the initial or final state by resonant interaction with the colliding (identical) ground-state atoms. The sudden approximation method allows us to take into account correctly the magnetic sublevels of the interacting state. From our discussion at the end of Sec. II, it is clear that in this case the cross section is given by

$$\sigma = 2\pi \int \text{Re} \left\{ 1 - \frac{1}{3} [\langle 1|T|1\rangle + \langle 0|T|0\rangle + \langle -1|T|-1\rangle] \right\} b db.$$

The states $|1\rangle$, $|0\rangle$, $|-1\rangle$ are the magnetic sublevels of the state which has the interaction with the ground state. The T matrix for the other state is, of course, just the unit matrix if that state has no interaction with the ground state. We have assumed a state with $J=1$ for convenience, but the general case is exactly the same, except that the dimension of the matrix to be diagonalized may be greater. Using the matrix elements calculated before for the $J=1$ resonant case, we get

$$\sigma = \frac{4\pi}{3} \int_0^\infty \left(1 - \cos \frac{\alpha}{b^2} \right) b db = \frac{8\pi}{3} \int_0^\infty \sin^2 \frac{\alpha}{2b^2} b db.$$

We note that the sum of the diagonal elements of the T matrix is independent of the Euler angles, as we should expect, since in the limit of the magnetic field going to zero (optical case), the angular average should not be necessary because of the isotropy of space. The indicated integration is readily performed to yield

$$\sigma = \frac{\pi r_0 c \lambda f}{6 \bar{v}}, \quad (18)$$

where λ and f refer to the *resonant* transition to the *ground* state. Recently, Kuhn and Vaughan¹⁹ have measured the broadening of lines terminating in the lowest 1P_1 state of helium. This state is connected to the ground state by the 584-Å line which has an oscillator strength of 0.38 ($\pm 10\%$) as measured by Kuhn and Vaughan.¹⁹ Using this value, the half-width due to broadening is, by Eq. (18),

$$\Delta_{1/2} = \frac{n \bar{v} \sigma}{\pi} = (0.31 \pm 0.03) \times 10^{-8} n \text{ cps.}$$

¹⁹ H. Kuhn and W. Vaughan (to be published). We wish to thank Professor Kuhn for communicating his results to us before publication.

Kuhn and Vaughan found for the transition 2^1-3^1S at 7281 Å case,

$$\Delta_{1/2} = (0.27 \pm 0.02) \times 10^{-8} n \text{ cps}$$

$$\sigma = \frac{4\pi r_0 c \lambda f}{15 \bar{v}}$$

—in excellent agreement with our result. They also verified over a wide range of temperatures and densities that the broadening is independent of velocity and linear in density, as predicted. It is thus seen that the general theory developed above explains very well the results of optical resonant broadening, as well as accounting for the apparent anomalous behavior of the cross section for self-broadening of double resonance lines in cadmium and zinc and foreign gas broadening of double resonance lines in mercury. The second-order effects in the double resonance cases are necessarily treated in a rather approximate manner, although the expression for the first-order resonant effect—in this

—should be quite accurate. Unfortunately, no reliable measurements have been made on double resonance curves at sufficiently high densities in the case of moderately large oscillator strengths. Mercury ($f=0.025$) is a good example of such a case, and a measurement here would be of interest.

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