

## Resonant Broadening of Double-Resonance and Level-Crossing Signals: Application to the $^3P_1$ State in Mercury

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A detailed calculation of the relaxation matrix of resonance atomic states by resonant collisions is carried out in the semiclassical impact theory. The validity of the different approximations is discussed. These results have been tested by observing self-broadening of level-crossing curves in high field and in zero field, in the  $6^3P_1$  state in mercury. Observation of these signals at high pressures is very difficult with a pure isotope because of strong absorption and trapping of resonance light in the vapor; it is made very easy by observing level-crossing signals of one isotope in a very low concentration in the vapor of another isotope. Collisions between the different pairs of mercury isotopes have been thus systematically studied. Results are in excellent agreement (10%) with theory, both for the absolute value of cross sections and for the ratio of orientation broadening to alignment broadening.

### I. INTRODUCTION

EVER since the work of Holtzmark in 1925, resonance broadening (or self-broadening) of optical resonance lines has been the subject of many publications. It occurs when an atom in a resonance state is perturbed by identical atoms in the ground state: The dipole-dipole interaction allows resonant exchange of excitation between them. At low pressures two-body interactions are predominant and a collision (impact) approximation is well justified. Because the interaction is resonant, the corresponding cross section is very large, and it is a good approximation to assume that during their collision the two atoms follow straight lines. It is then possible to calculate self-broadening of optical lines in a semiclassical way. Most of the different theories which have been proposed are simple, and are substantially equivalent to the work of Furssov and Wlassow<sup>1</sup> in 1936.

More recently, Byron and Foley<sup>2</sup> extended these theories to self-broadening of magnetic-resonance lines of the excited state (double resonance). In a previous paper<sup>3</sup> (see also D'yakonov and Perel<sup>4</sup>), one of the writers has shown how it is possible to extend their method in a systematic way—making use of the density-matrix formalism—to describe completely the relaxation of the different observables of the excited atomic state, and also the broadening of the different level-crossing and double-resonance signals.

It is generally a good approximation to assume that the atoms are classical particles, and also that the signals of interest can be described by a density matrix involving the internal atomic states only, independent of the atomic position and velocity. In doing so one neglects correlations between the states of the two atoms in-

volved in a collision (see Ref. 5). In the problem considered here this density matrix  $\sigma$  obeys a rate equation of the type

$$\frac{d\sigma}{dt} = -i[\mathcal{H}, \sigma] - i\langle \mathfrak{M} \rangle \sigma + \left( \frac{d\sigma}{dt} \right)_p, \quad (1)$$

where  $\mathcal{H}$  is the atomic Hamiltonian,  $(d\sigma/dt)_p$  represents the action of the external "pump", and  $\langle \mathfrak{M} \rangle$  is a "relaxation matrix" acting in "Liouville space"<sup>6,7</sup> (i.e., the vectorial space of the operators of the usual atomic-state space),  $\sigma$  being a vector in Liouville space. As a rule,  $\langle \mathfrak{M} \rangle$  is independent of time; if the same is true of  $\mathcal{H}$  and  $(d\sigma/dt)_p$ , the stationary state of the system is simply obtained by putting  $d\sigma/dt=0$  in Eq. (1).

Equation (1) is a straightforward generalization of the Bloch equations, and also of the basic equation of the optical-pumping cycle theory of Cohen-Tannoudji and Barrat.<sup>8</sup> A large class of relaxation processes gives a similar rate equation. Section II of the present paper recalls the essential properties of  $\langle \mathfrak{M} \rangle$ , taking into account the spherical symmetry of the relaxation process (by the dipole-dipole interaction). The first purpose of this paper is to report a numerical calculation of the relaxation matrix for resonant broadening (Sec. III), using the general semiclassical impact theory. Section IV is devoted to a brief discussion of validity and possible extensions of this theory. In Sec. V, we report experimental results of self-broadening in the first  $^3P_1$  state of mercury. The observation of the pure resonance broadening in a pure isotope of mercury is prevented by the very strong absorption of the resonance light in the vapor which leads, in particular, to multiple scattering

<sup>1</sup> W. Furssov and A. Wlassow, *Physik Z. Sowjetunion* **10**, 378 (1936).

<sup>2</sup> F. W. Byron, Jr., and H. M. Foley, *Phys. Rev.* **134**, A625 (1964).

<sup>3</sup> A. Omont, *J. Phys. (Paris)* **26**, 26 (1965).

<sup>4</sup> M. I. Dyakonov and V. I. Perel, *Zh. Eksperim. i Teor. Fiz.* **48**, 345 (1965) [English transl.: *Soviet Phys.—JETP* **21**, 227 (1965)].

<sup>5</sup> A. Omont, thesis, Paris, 1967, CNRS Microfilm No. AO 1341 (unpublished). This microfilm is available by writing to CNRS, 15 Quai Anatole France, Paris 7, France.

<sup>6</sup> U. Fano, *Rev. Mod. Phys.* **29**, 74 (1957); *Phys. Rev.* **131**, 259 (1963); **133**, B828 (1964).

<sup>7</sup> A. Ben Reuven, *Phys. Rev.* **141**, 34; **145**, 7 (1966).

<sup>8</sup> C. Cohen-Tannoudji, *Ann. Phys. (Paris)* **7**, 423, 469 (1962); J. P. Barrat and C. Cohen-Tannoudji, *J. Phys. Radium* **32**, 329 (1961); **32**, 443 (1961).

(responsible for coherence narrowing) (see Ref. 5). We have avoided this effect by observing the broadening of the level-crossing curves of the atoms of one isotope of low concentration mixed with another isotope of high concentration. Experimental results agree very well with theory. In Sec. VI, we compare also the present theory with other available experimental results. A more detailed account of all theoretical and experimental results can be found in two unpublished theses.<sup>5,9</sup>

## II. GENERAL PROPERTIES OF THE RELAXATION MATRIX $\langle \mathfrak{N} \rangle$

### A. Rotational Invariance

Relaxation processes are often invariant under space rotations. It is then very convenient to write  $\langle \mathfrak{N} \rangle$  in an irreducible representation of Liouville space.<sup>6,7,10</sup> We write the components of such a basis

$$F_{\alpha} G_{\beta} T_{q}^{(k)} = \sum_{mn} (-)^{G-n} \langle F G m - n | k q \rangle \times |\alpha F m \rangle \langle \beta G n |, \quad (2)$$

where  $|\alpha F m \rangle$  are basis vectors of the standard irreducible representation in wave-vector space,  $F$  is the total angular momentum,  $m$  is its projection on a space-fixed axis  $Oz$ , and  $\alpha$  is a shorthand notation for all other quantum numbers.  $\langle F G m - n | k q \rangle$  is a Clebsch-Gordan coefficient.<sup>11</sup>  $F_{\alpha} G_{\beta} T_{q}^{(k)}$  is then a standard component of an irreducible tensorial operator of wave-vector space.

In this representation the density matrix can be written

$$\sigma = \sum_{\alpha F \beta G k q} F_{\alpha} G_{\beta} S_{\alpha}^k F_{\alpha} G_{\beta} T_{q}^{(k)}. \quad (3)$$

Using the orthogonality and normalization relations of the tensors  $F_{\alpha} G_{\beta} T_{q}^{(k)}$  and  $F'_{\alpha'} G'_{\beta'} T_{q'}^{(k')}$ , one gets

$$F_{\alpha} G_{\beta} S_{\alpha}^k = \langle F_{\alpha} G_{\beta} T_{q}^{(k)} | q \rangle. \quad (4)$$

The coefficient  $F_{\alpha} G_{\beta} S_{\alpha}^k$  then represents the  $q$ th component of the  $k$ th multipole moment of the atoms; for instance, for  $k=1$  it is one of the three components of the dipole moment (or "orientation"), and for  $k=2$  it is one of the five components of the quadrupole moment (or "alignment").

When  $\langle \mathfrak{N} \rangle$  is invariant under rotations, it is a scalar operator in Liouville space, and it follows that one may write

$$\langle \mathfrak{N} \rangle F_{\alpha} G_{\beta} T_{q}^{(k)} = -i \sum F_{\alpha} G_{\beta} F'_{\alpha'} G'_{\beta'} g^k F'_{\alpha'} G'_{\beta'} T_{q'}^{(k)}. \quad (5)$$

These coefficients  $g^k$  are independent of  $q$ . They are the only nonzero terms of  $\langle \mathfrak{N} \rangle$ . The real part of  $g^k$  is a relaxation rate of transfer or of destruction of population ( $k=0$ ), orientation ( $k=1$ ), alignment ( $k=2$ ), etc.: It is the same for the different  $q$  components. The real

part of  $\langle \mathfrak{N} \rangle$  is related to shifts in the observed resonance frequencies of atomic transitions.

### B. Transition 1-0

We now calculate  $\langle \mathfrak{N} \rangle$  for resonance broadening for an atom in which the angular momentum of the ground state  $g$  is zero and the angular momentum of the excited state  $e$  is equal to 1.

We suppose first that it is possible to distinguish between the atoms under observation, called 1, and the perturbers, called 2. (For instance, one can study a level-crossing signal of an isotope, 1, perturbed by collisions with atoms of another isotope, 2, of the same element; see Sec. V.) Because the number of excited atoms is very small, interactions between excited atoms can be neglected completely. We then assume that either no atom is excited or only one atom is excited. The excited atom may belong to class 1 or to class 2. Such a system of two atoms, one of each class, has seven substates: one when both atoms are in the ground state, three when atom 1 is excited and atom 2 is unexcited, and three when atom 2 is excited and atom 1 is in the ground state. Therefore the density matrix  $\sigma$  representing such a state of the vapor has 49 elements. Because we ignore correlations between atom 1 and atom 2 (see Ref. 5), we are only interested in the following density matrices (16 elements):

$$\begin{aligned} \sigma_1 &= \text{Tr}_2 \sigma, \\ \sigma_2 &= \text{Tr}_1 \sigma, \end{aligned} \quad (6)$$

where  $\text{Tr}_i$  means partial trace operation in the subspace of atom  $i$ . We can write with no ambiguity

$$\sigma_i = \sum_{\alpha \beta k q} \alpha_{\beta} S_{\alpha}^k(i) \alpha_{\beta} T_{q}^{(k)}(i), \quad (7)$$

where  $\alpha$  and  $\beta$  are  $e$  or  $g$ . The meaning of  $\alpha_{\beta} S_{\alpha}^k(i)$  is clear. For instance,  ${}_{ee}S_0^0(i)$  is the total probability of excitation (population) of atoms  $i$ ,  ${}_{ee}S_1^1(i)$  is the  $q$ th component of the "orientation" of the excited state of  $i$ , and  ${}_{eg}S_1^1(i)$  is the  $q$ th component of the (electric) dipole moment (or "optical coherence") between excited and ground state of  $i$ , etc.

Equation (5) then takes the following form (except when  $\alpha\beta = gg$ ):

$$\begin{aligned} -i \langle \mathfrak{N} \rangle_{\alpha \beta} T_{q}^{(k)}(1) &= -\alpha_{\beta} g^k(1) \alpha_{\beta} T_{q}^{(k)}(1) \\ &\quad - \alpha_{\beta} g^k(2) \alpha_{\beta} T_{q}^{(k)}(2). \end{aligned} \quad (8)$$

We shall see in Sec. III that every  $\alpha_{\beta} g^k(i)$  [except  ${}_{eg}g^1(2)$ ] is *real*, so that  $1/{}_{eg}g^k(1)$  is the relaxation time of the "population" ( $k=0$ ), of the "orientation" ( $k=1$ ), or of the "alignment" ( $k=2$ ) of the excited state of atoms 1. Similarly,  $1/{}_{eg}g^1(1)$  is the relaxation time of optical coherence of atoms 1.  $-\alpha_{\beta} g^k(2)$  gives the probability and the phase factor of the transfer of the same quantities from atom 1 to atom 2.

If atoms 1 and 2 are indistinguishable, it is not possible to observe independently  $\alpha_{\beta} S_{\alpha}^k(1)$  and  $\alpha_{\beta} S_{\alpha}^k(2)$ ,

<sup>9</sup> J. Meunier, thesis, Paris, 1966 (unpublished).

<sup>10</sup> U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

<sup>11</sup> A. Messiah, *Mécanique Quantique* (Dunod Cie., Paris, 1959).

but only  $\alpha\beta s^k_g(1) + \alpha\beta s^k_g(2)$ . The corresponding relaxation rate (due to resonant collision) of the excited state of the vapor is then

$$ee g^k(1+2) = ee g^k(1) + ee g^k(2). \quad (9)$$

It is clear that  $ee g^0(1+2) = 0$ .

We first recall in Sec. III the semiclassical method used to calculate the different  $\alpha\beta g^k(i)$ . We will discuss the results of their numerical calculation in Sec. IV.

### III. OUTLINE OF THE CALCULATION OF $\langle \mathfrak{M} \rangle$

The semiclassical impact theory is simple in its principles and is now fairly well known.<sup>1,4,12,13</sup> There are three steps in the calculation of the relaxation matrix  $\langle \mathfrak{M} \rangle$ :

(a) Knowing the interaction potential  $V(\mathbf{R})$  for every interatomic position  $\mathbf{R}$ , one solves the Schrödinger equation for a collision with given parameters. The change in the state vector during the collision defines the collision matrix  $S$ . This matrix has been derived in Ref. 3 by several approximation methods. We give here the result of a more precise numerical calculation.

(b) The effects of one collision are averaged over all directions of the relative velocity  $\mathbf{v}$  and of the impact parameter  $\mathbf{b}$ , assuming a random distribution of their orientations (see Ref. 3).

(c) Integration with respect to the impact parameter  $b$ : The approximate expressions of  $S$  derived in Ref. 3 are not valid for small  $b$  values, and some rather crude approximations are necessary to obtain the relaxation matrix. This difficulty is almost completely avoided with a numerical calculation valid and precise even for rather small  $b$  values (strong collisions).

#### A. Collision Matrix

In this section, we consider the change in the state vector  $|\psi\rangle$  of two atoms, because of a collision having a given  $\mathbf{v}$  and  $\mathbf{b}$ . The vector  $|\psi\rangle$  has seven components (see Sec. II B). We define a three-component vector

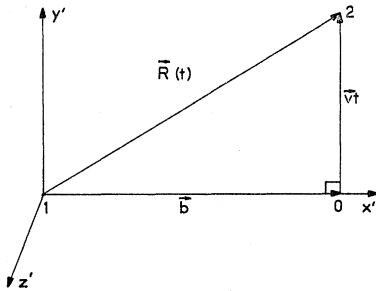


FIG. 1. Collision coordinates.

<sup>12</sup> P. W. Anderson, Phys. Rev. **76**, 647 (1949); **86**, 809 (1952).

<sup>13</sup> J. M. Winter, in *Optics and Quantum Electronics*, edited by C. DeWitt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach Science Publishers, Inc., New York, 1964).

$|A_1\rangle$  with the three components of  $|\psi\rangle$  corresponding to atom 1 excited and atom 2 unexcited. Similarly, the three-component vector  $|A_2\rangle$  represents the system when atom 2 is excited and atom 1 is unexcited.

The dipole-dipole interaction potential is

$$V(\mathbf{R}) = R^{-3} \mathbf{P}_1 \cdot \mathbf{P}_2 - 3R^{-5} (\mathbf{P}_1 \cdot \mathbf{R})(\mathbf{P}_2 \cdot \mathbf{R}), \quad (10)$$

where  $\mathbf{P}_i$  is the electric-dipole operator of atom  $i$ . Because of this particular form of  $V$ , the Schrödinger equation can be reduced to [Ref. 3, Eq. (8)]

$$\frac{d}{dt} |A_1(t)\rangle = -iV(t) |A_2(t)\rangle, \quad (11)$$

$$\frac{d}{dt} |A_2(t)\rangle = -iV(t) |A_1(t)\rangle,$$

with  $\hbar = c = 1$ .

Assuming that the relative trajectory is a straight line,  $V(t)$  is determined for each time  $t$  by the relation (see Fig. 1)

$$\mathbf{R}(t) = \mathbf{b} + \mathbf{v}t. \quad (12)$$

It is fairly easy to derive explicitly the elements of the  $3 \times 3$   $V(t)$  matrix; it is convenient to formally write this matrix in the form

$$V = p(J_{\mathbf{R}}^2 - \frac{1}{3}J^2), \quad (13)$$

where  $J_{\mathbf{R}}$  is the matrix of the projection on the  $\mathbf{R}$  direction of an angular momentum  $\mathbf{J}$ , with  $J = 1$ , and

$$p = -\frac{3}{2} \frac{e^2 f}{mk_0 R^3} = -\frac{9}{4} \frac{\Gamma}{k_0^3 R^3}, \quad (14)$$

where  $e$  and  $m$  are the electronic charge and mass, respectively,  $k_0$  is the energy of the resonance transition,  $f$  is its absorption oscillator strength, and  $\tau = \Gamma^{-1}$  is the lifetime of the excited state of a single atom.

We assume that atom 1 is excited before the collision ( $t = -\infty$ )  $|A_2(-\infty)\rangle = 0$ , and we define the collision matrices  $S_1(\mathbf{b}, \mathbf{v})$  and  $S_2(\mathbf{b}, \mathbf{v})$  by

$$|A_1(\infty)\rangle = S_1(\mathbf{b}, \mathbf{v}) |A_1(-\infty)\rangle, \quad (15)$$

$$|A_2(\infty)\rangle = S_2(\mathbf{b}, \mathbf{v}) |A_1(-\infty)\rangle.$$

It is convenient to rewrite system (11) in terms of the following dimensionless parameters:

$$x = vt/b, \quad (16)$$

$$q = p \frac{R^3}{b^2 v} = -\frac{9}{4} \frac{\Gamma}{k_0^3 b^2 v} = -\frac{3}{2} \frac{e^2 f}{mk_0 b^2 v}, \quad (17)$$

$$\frac{d}{dx} |A_1\rangle = -iq(1+x^2)^{-3/2} (J_{\mathbf{R}}^2 - \frac{1}{3}J^2) |A_2\rangle, \quad (18)$$

$$\frac{d}{dx} |A_2\rangle = -iq(1+x^2)^{-3/2} (J_{\mathbf{R}}^2 - \frac{1}{3}J^2) |A_1\rangle.$$

It is not possible to solve this system exactly.

For small  $q$  (large  $b$ ) one finds the first terms of the perturbation developments of  $S_1$  and  $S_2$  (Ref. 3):

$$S_2^{as} = -i \int_{-\infty}^{+\infty} V(t) dt = -\frac{1}{3} i 2q (J_{x'}^2 - J_{z'}^2),$$

$$S_1^{as} = 1 - \int_{-\infty}^{+\infty} dt \int_{-\infty}^t dt' V(t) V(t')$$

$$= 1 - q^2 \left( \frac{2}{9} J_{y'}^2 - \frac{\pi}{12} i J_{z'} \right), \quad (19)$$

where the collision axes  $x'$ ,  $y'$ ,  $z'$  are defined in Fig. 1.

Some authors<sup>2,12</sup> use the approximation in which one neglects the commutators  $[V(t), V(t')]$ , which indeed are different from zero for  $t \neq t'$ . This is a poor approximation for large  $q$ 's (see Sec. IV). It gives

$$S_1^s = \cos(iS_2^{as}),$$

$$S_1^s = -i \sin(iS_2^{as}). \quad (20)$$

The general properties of system (18) are discussed in detail in Ref. 5. It is simpler to take the combinations  $(1/\sqrt{2})(|A_1\rangle \pm |A_2\rangle)$  instead of  $|A_1\rangle$  and  $|A_2\rangle$  in order to get two  $3 \times 3$  independent systems. If the quantization axis is parallel to  $Oz'$  (see Fig. 1), the matrix elements of the interaction potential  $V(t)$  are zero between the  $m=0$  Zeeman sublevel and the sublevels  $m=\pm 1$ ; each of these  $3 \times 3$  systems is then reduced to an independent equation plus a  $2 \times 2$  system.<sup>5,14</sup>

We have solved these systems by a numerical extrapolation method for 90 values of  $q$  between 0 and 9, using an IBM 1620 computer. Watanabe<sup>14</sup> has recently calculated the same quantities by an iteration method. As we shall see in Sec. IV A, his results are very similar to ours.

This numerical calculation becomes prohibitive for very large  $q$  ( $q > 10$ ). In that range it is possible to use an adiabatic approximation<sup>5,11,15</sup> if one assumes that the interaction is so strong that during the collision the atomic states adiabatically follow the rotating axes.

## B. Angular Averages

For a collision of given  $\mathbf{b}$  and  $\mathbf{v}$ , we write the density matrices after the collision in the form

$$\sigma_1(\infty) = Y_1(\mathbf{b}, \mathbf{v}) \sigma_1(-\infty) = \tilde{S}_1 \sigma_1(-\infty) \tilde{S}_1^\dagger,$$

$$\sigma_2(\infty) = Y_2(\mathbf{b}, \mathbf{v}) \sigma_1(-\infty) = \tilde{S}_2 \sigma_1(-\infty) \tilde{S}_2^\dagger.$$

$Y_i(\mathbf{b}, \mathbf{v})$  are matrices representing Liouville space transformations;  $\tilde{S}_i$  are extensions of  $S_i$ , taking into account the fact that the state in which both atoms are in their ground state is not perturbed by the collision

$$\tilde{S}_i = S_i + |1g, 2g\rangle \langle 1g, 2g|. \quad (21)$$

<sup>14</sup> Tsutomu Watanabe, Phys. Rev. **138**, A1573; **140**, AB5 (1965).  
<sup>15</sup> V. N. Rebane and T. W. Rebane, Opt. Spectry. **20**, 185 (1966).

The matrices  $\langle Y_i(\mathbf{b}, \mathbf{v}) \rangle$  obtained after an angular average with respect to a random distribution of the orientation of  $\mathbf{b}$  and  $\mathbf{v}$  (with  $\mathbf{b} \cdot \mathbf{v} = 0$ ) are invariant under rotations, and they have the same properties as  $\langle \mathfrak{M} \rangle$  (Sec. II B). We then write ( $\alpha\beta \neq gg$ )

$$\langle Y_i(\mathbf{b}, \mathbf{v}) \rangle_{\alpha\beta} T^{(k)}_q(1) = \delta_{i1} \alpha\beta T^{(k)}_q(1) - \alpha\beta \Pi^k(i; b, v) \alpha\beta T^k_q(i), \quad (22)$$

where the quantities  $\alpha\beta \Pi^k(i; b, v)$  are pure numbers.  $\alpha\beta \Pi^k(1; b, v)$  are the mean probabilities that, in a collision with given  $b$  and  $v$ , the excitation ( $\alpha\beta = ee$ ,  $k=0$ ), orientation ( $\alpha\beta = ee$ ,  $k=1$ ), alignment ( $\alpha\beta = ee$ ,  $k=2$ ), or optical coherence ( $\alpha\beta = eg$ ) of atom 1 are destroyed.  $\alpha\beta \Pi^k(2; b, v)$  are the mean probabilities—multiplied by the right phase factor—that these same quantities are transferred to atom 2.

Using irreducible-tensorial-sets techniques, one finds the following expressions<sup>2,5</sup>:

$$e_g \Pi^1(i; b, v) = \delta_{i1} - \frac{1}{3} \langle \text{Tr}[S_i(\mathbf{b}, \mathbf{v})] \rangle, \quad (23)$$

$$e_e \Pi^k(i; b, v) = \delta_{i1} - \sum_{\chi\sigma} (-)^{k+\chi} \begin{Bmatrix} 1 & 1 & k \\ 1 & 1 & \chi \end{Bmatrix} \times |\text{Tr}[S_i^\dagger e_e T^{(\chi)}_\sigma]|^2, \quad (24)$$

where the quantity inside the brackets is a  $6-j$  Wigner coefficient.<sup>11</sup>

By taking  $S_i = S_i^{as}$ , one gets to first order in  $q^2$

$$e_e \Pi^k_{as}(1) = 2e_g \Pi^1_{as}(1) = -e_e \Pi^0_{as}(2) = 2e_e \Pi^1_{as}(2)$$

$$= -10e_e \Pi^2_{as}(2) = 8q^2/27, \quad (25)$$

$$e_g \Pi^1_{as}(2) = 0.$$

We have plotted these quantities in Figs. 2–6 (dashed lines), together with the values derived from the numerical calculation of  $S_i$  (Sec. III A).

For very large  $q$  (collision at very small distances) one may assume in an intuitive way that on the average the collision completely destroys the orientation, alignment, and optical coherence of the system:

$$\alpha\beta^0 \Pi^{1,2}(i) = \delta_{i1}, \quad (26)$$

and that the probability of excitation is the same for

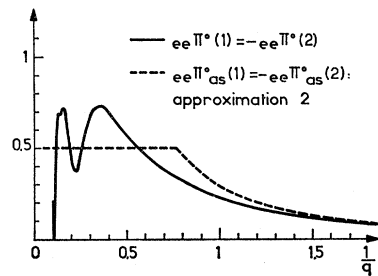


FIG. 2. Probability of excitation transfer versus square of the impact parameter  $[q = 9\Gamma/(4k^2vb^2)]$ .

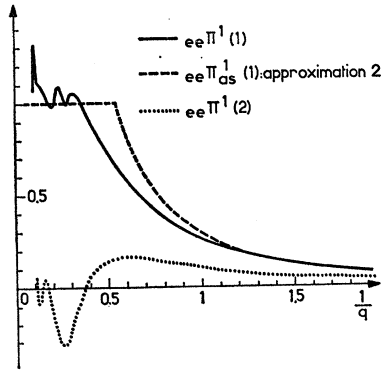


FIG. 3. "Probabilities" of destruction and transfer of orientation.

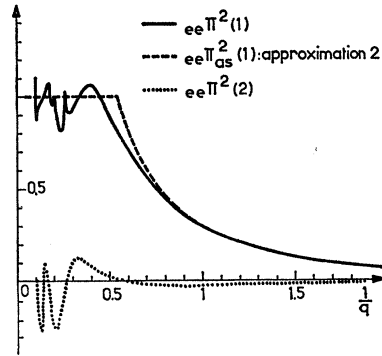


FIG. 4. "Probabilities" of destruction and transfer of alignment.

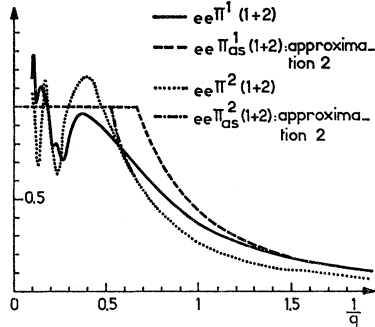


FIG. 5. "Probabilities" of destruction of total orientation and total alignment.

both atoms after the collision:

$$ee^0\Pi^0(1) = -ee^0\Pi^0(2) = \frac{1}{2}. \quad (27)$$

This is in qualitative agreement with our results (Figs. 2-6). The value we obtain oscillates around values of the above magnitude for large  $q$ . We wish to point out, nevertheless, that the adiabatic approximation leads to results which are slightly different from  $\alpha_\beta^0\Pi^k(i)$ , but which are also in agreement with the numerical computation.

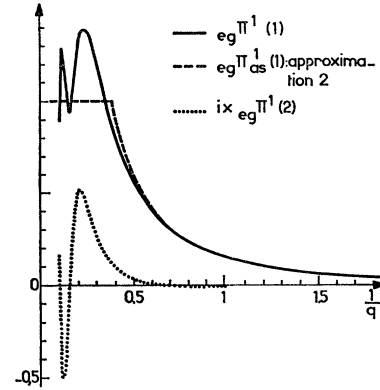


FIG. 6. "Probabilities" of destruction and transfer of "optical coherence."

### C. Relaxation Rates

The probability that a collision with a given  $v$  and  $b$  occurs during the time  $dt$  is equal to  $N_2 v dt 2\pi b db$ ,  $N_2$  being the number of perturbers per unit volume. The relaxation rates are then simply related to  $\alpha_\beta\Pi^k(i; b, v)$  by the relation

$$\alpha_\beta g^k(i) = 2\pi N_2 v \int_0^\infty \alpha_\beta \Pi^k(i; b, v) b db. \quad (28)$$

As is well known for an  $R^{-3}$  interaction,  $\alpha_\beta g^k(i)$  is independent of  $v$ , and one need not perform an average on velocities. To conform to previous notations,<sup>16,17</sup> we introduce the numerical parameters

$$\alpha_\beta K^k(i) = \frac{2}{\sqrt{3}} \int_0^\infty \alpha_\beta \Pi^k(i; q) d(1/q), \quad (29)$$

with

$$\alpha_\beta g^k(i) / \alpha_\beta K^k(i) = \frac{\pi e^2 f N_2}{\sqrt{3} m k_0} = \pi \frac{1}{2} \sqrt{3} \frac{\Gamma N_2}{k_0^3}. \quad (30)$$

The results obtained for  $\alpha_\beta K^k(i)$  are given in Table I for different approximations. (The approximations 1 and

TABLE I. Relative magnitude of relaxation rates.  $\alpha_\beta K^k(i)$  is defined in Eqs. (29) and (30).

Approximation	1	2	3	
$eeK^0(1)$	1.81 $[\pi/\sqrt{3}]$	2	1.94	1.96 <sup>a</sup>
$eeK^1(1+2)$	3.63 $[2\pi/\sqrt{3}]$	3.45 $[2\sqrt{3}]$	3.06	3.2 <sup>b</sup>
$eeK^2(1+2)$	2.18 $[6\pi/5\sqrt{3}]$	2.68	2.63	2.6 <sup>b</sup>
$eeK^1(1)$	2.73 $[3\pi/2\sqrt{3}]$	2.83 $[2\sqrt{2}]$	2.57	
$eeK^2(1)$	2.00 $[11\pi/10\sqrt{3}]$	2.83 $[2\sqrt{2}]$	2.72	
$egK^1(1)$	1.81 $[\pi/\sqrt{3}]$	2	2.07	
$egK^1(2)$	0.91 $[\pi/2\sqrt{3}]$	...	+0.49	
$egK^2(2)$	0.18 $[\pi/10\sqrt{3}]$	...	-0.09	
$-ie_gK^1(2)$	0	...	0.07	

<sup>a</sup> Reference 14.  
<sup>b</sup> Reference 4.

<sup>16</sup> A. W. Ali and H. R. Griem, Phys. Rev. **140**, A1044 (1965); **144**, 366 (1966).

<sup>17</sup> A. Omont, Compt. Rend. **262**, 190 (1966).

2 used here are the same as Anderson's approximations 1 and 2.<sup>12</sup>) The definition of the different approximations are the following:

Approximation 1:  $S_i = S_i^*$  [Eq. (20)]. One neglects the commutators  $[V(t), V(t')]$ .

Approximation 2 ( $i=1$  or  $i=1+2$ ; see Figs. 2-6):

$${}_{\alpha\beta}\Pi^k(i; q) = {}_{\alpha\beta}\Pi^k{}_{as}(i; q) \quad \text{for } q \leq q^{\sim k}_i, \quad (31)$$

$${}_{\alpha\beta}\Pi^k(i; q) = {}_{\alpha\beta}{}^0\Pi^k(i) \quad \text{for } q \geq q^{\sim k}_i. \quad (32)$$

$q^{\sim k}_i$  is defined in a way similar to that of the "Weisskopf radius," by

$${}_{\alpha\beta}\Pi^k{}_{as}(i, q^{\sim k}_i) = {}_{\alpha\beta}{}^0\Pi^k(i). \quad (33)$$

Approximation 3:

$${}_{\alpha\beta}\Pi^k(i; q) = {}_{\alpha\beta}{}^0\Pi^k(i) \quad \text{for } q \geq 9.$$

For  $q < 9$  one uses the results of our numerical calculation (see Figs. 2-6).

#### IV. DISCUSSION AND EXTENSIONS

##### A. Mathematical Discussion

Several of the  ${}_{\alpha\beta}K^k(i)$  coefficients have been calculated by different authors, using approximations 1 or 2 or a numerical calculation. A correct use of approximations 1 or 2 leads, of course, to exactly the same results as those of Table I:  ${}_{ee}K^0(1)$  has been calculated in this way by Holstein *et al.*<sup>18</sup> in approximation 2, and  ${}_{eg}K^1(1)$  by Ali and Griem<sup>16</sup> in approximation 2 and by Byron and Foley<sup>2</sup> in approximation 1. These last authors have also evaluated  ${}_{ee}K^2(1+2)$  in approximation 1, but their result (2.90) is slightly different from the exact one (2.18), since they neglected the coupling induced by collisions between, for instance,  ${}_{ee}\sigma_{10}(1)$  and  ${}_{ee}\sigma_{0-1}(2)$ . (These density-matrix elements are written here in the usual atomic-state representation.)

In column 4 of Table I are given results of different numerical calculations. As a rule, the agreement with our results is good. The small differences which appear can be explained by lack of accuracy of the numerical resolution of the collision-equation system, or of the approximation necessary for small  $b$  values.

When compared with the above more rigorous results of the numerical resolution (approximation 3), those of approximation 2 appear rather good: The areas below the solid-line and dashed-line curves of Figs. 2-6 are approximately equal. On the contrary, the accuracy of approximation 1 is as a rule rather poor.

##### B. Extensions

One may find in Ref. 5 the following extensions of the above theory:

(a) Effect of a nuclear spin  $I$ , for a transition in which the electronic angular momentum is  $J_g = 0$  in the ground

<sup>18</sup> T. Holstein, D. Alpert, and A. O. McCoubrey, *Phys. Rev.* **85**, 985 (1952).

state and  $J_e = 1$  in the excited state. One assumes that the hyperfine interaction is small enough to be neglected during the collision which perturbs only the electronic part of the atomic-state vector. Then, knowing this perturbation (Sec. III), one is just left with a problem of recoupling angular momenta. New parameters have to be introduced: for instance, transfer probabilities for population, orientation, etc., between the different hyperfine components of both atoms, influence of resonant collisions on the relaxation rates of nuclear orientation in the ground state, broadening of level-crossing curves, etc. Numerical evaluations of these quantities are given in Ref. 5.

(b) Determination in approximation 2 of the different relaxation rates for *any values of the angular momenta* of the excited state  $F_e$  and of the ground state  $F_g$ , when these states are far away from any other level with a different  $F$ .

(c) If the different sublevels of both atoms are far from resonance, the existence of these energy separations changes the relaxation rates: In particular, in Ref. 5, one considers the energy separations corresponding to an isotope shift and to a Zeeman effect in a strong magnetic field, and their influence is evaluated by an extension of the methods of Tsao and Curnutte.<sup>19</sup>

(d) It is possible to replace the "static" dipole potential of Sec. III by the complete dipole-dipole interaction<sup>20</sup> including "radiative" terms, and to calculate in this way the relaxation rates. This procedure clarifies the relations between resonant collisions and multiple scattering due to imprisonment of resonance radiation,<sup>21</sup> but some difficult problems exist which have not been solved rigorously.

##### C. Physical Signals

In Ref. 5, we have discussed in some detail the different approximations made in Sec. III: use of single-atom density matrices, description of the collision in terms of classical particles, straight-line path, resonant electrostatic dipole potential, etc. It appears that this model is as a rule fairly good for the quantities related only to the excited state (or only to the ground state), i.e., to double resonance, level crossing, etc. For instance, the inaccuracy is estimated to be less than 10% for the  $6^3P_1$  state in mercury. In that case, it is also a very good approximation to assume that resonant collisions are a relaxation process independent of other processes (spontaneous emission, multiple scattering of resonance radiation, etc.). Accordingly, one may trust this theory to predict very accurately the self-broadening constants of the different double-resonance and level-crossing lines.

<sup>19</sup> C. J. Tsao and B. Curnutte, *J. Quant. Spectry. Radiative Transfer* **2**, 41 (1962).

<sup>20</sup> M. J. Stephen, *J. Chem. Phys.* **40**, 669 (1964); M. R. Philpott, *Proc. Phys. Soc. (London)* **89**, 217 (1966).

<sup>21</sup> J. P. Barrat, *J. Phys. Radium* **20**, 541 (1959); **20**, 633 (1959); **20**, 657 (1959).

For optical lines a simple approximation is to assume that in the presence of self-broadening the line remains an unshifted Voigt profile, with a Lorentzian width enlarged by an amount equal to  $\epsilon_0 g^1(1)$ .

We think that as a rule this is a good approximation for transitions between a resonance level and an upper excited level (see Sec. VI A). The problem is much more complicated for the resonance line itself, because of atomic motion (Doppler broadening, etc.) and atomic correlations [transfer of optical coherence related to  $\epsilon_0 g^1(2)$ , etc.]. In some cases,<sup>22</sup> it is possible that the actual line profile differs in an appreciable way from the simple unshifted Lorentzian line related to  $\epsilon_0 g^1(1)$ .

## V. OBSERVATION AND MEASUREMENT OF THE SELF-BROADENING OF THE $6^3P_1$ STATE IN MERCURY

### A. Experimental Method

Because of strong absorption and imprisonment of resonance radiation, the observation of the self-broadening of double-resonance and level-crossing signals is difficult in a typical case like the  $6^3P_1$  state of Hg. One needs a high Hg pressure ( $N\lambda^3 \sim 1$ ), and in this case resonance radiation is trapped to a high degree in the vapor of a pure isotope. This imprisonment tends to produce two well-known effects: narrowing of double-resonance and level-crossing lines and depolarization of resonance fluorescence emitted by the vapor. Then the double-resonance and level-crossing signals which are functions of the polarization of fluorescence become very poor, and the signal-to-noise ratio is too low to allow measurements with vapor pressures high enough to produce a significant broadening by collisions between identical atoms. Consequently, to observe this self-broadening one needs a "trick" which makes the effects of radiation trapping small in comparison with collision broadening.

Such a situation is realized for a pure (or concentrated) isotope in two cases where self-broadening has actually been observed:

(a) If the resonance transition has a small transition probability ( $^3P_1$  states of Cd or Zn), radiation trapping may be low when self-broadening is appreciable, because "nonresonant" collisions (related to van der Waals or dispersion interaction) which are nearly independent of the oscillator strength of the resonance transition studied become more important than "resonant" collisions.<sup>2,3,23</sup>

(b) In some cases, there are one or several intermediate levels (often metastable) between the excited and ground states, to which atoms in the excited state may decay. The photons emitted in this way are not

trapped in the vapor, for the population of such an intermediate level is as a rule too low. Consequently the fluorescence of the vapor is always fairly well polarized even at rather high pressure. Self-broadening of zero-field level crossing of  $(6s^26p7s) ^3P_1^0$  state in Pb has recently been measured in that way by Saloman and Happer.<sup>24</sup>

Neither of these conditions is found in the  $6^3P_1$  state of Hg. Attempts to measure self-broadening of double-resonance lines of that state in a concentrated isotope had lead to very imprecise results.<sup>21</sup> On the contrary, as we report here, it is possible to measure very accurately the broadening of level-crossing lines of one isotope *A* by atoms of another isotope *B*.

For this to be possible, it is sufficient that the relative partial vapor pressure of *A* be very small ( $\sim 10^{-3}$ ). Then, because the resonance photons of *A* cannot be absorbed by atoms *B*, one may find a pressure range at which the trapping of these photons is small enough, while broadening by collisions with atoms *B* is large.

### B. Results

Using the above technique, self-broadening of high-field level crossings was observed first.<sup>9,25</sup> The following crossings were investigated: ( $F = \frac{3}{2}$ ,  $m_F = -\frac{3}{2}$ ;  $F = \frac{1}{2}$ ,  $m_F = \frac{1}{2}$ ) of Hg<sup>199</sup> in nearly pure Hg<sup>198</sup>; ( $F = \frac{5}{2}$ ,  $m_F = \frac{5}{2}$ ;  $F = \frac{3}{2}$ ,  $m_F = \frac{1}{2}$ ), ( $F = \frac{3}{2}$ ,  $m_F = \frac{1}{2}$ ;  $F = \frac{3}{2}$ ,  $m_F = -\frac{1}{2}$ ) of Hg<sup>201</sup> in nearly pure Hg<sup>202</sup>.

The crossing fields are, respectively, 7100, 5200, and 4500 Oe.

The method was then extended<sup>5,26</sup> to zero-field level crossings (Hanle effect) with linear and circular optical polarizations which are related, respectively, to the alignment and the orientation of the excited state. The following measurements have been made: alignment and orientation of Hg<sup>200</sup> and Hg<sup>202</sup> in Hg<sup>198</sup>, Hg<sup>199</sup>, Hg<sup>201</sup>, and Hg<sup>204</sup>, and of Hg<sup>200</sup> in Hg<sup>202</sup>; alignment of the  $F = \frac{3}{2}$  hyperfine component of Hg<sup>199</sup> in Hg<sup>198</sup>, Hg<sup>202</sup>, and Hg<sup>204</sup>.

Because of the depolarizing factors of resonance radiation for the odd isotopes, the signal-to-noise ratio is, as a rule, better for the even isotopes (zero-field crossing) than for the odd isotopes. But high-field crossings have the advantage that they are well separated for the different odd isotopes. There is then no ambiguity in interpreting the experimental signal. In the zero-field case, on the contrary, one must be very careful to observe only the isotope of interest. This is realized by the use of several filters filled with very pure isotopes which absorb the spurious components of 2537 Å line emitted by the resonance cell or the excitation lamp. Consequently a much more important broadening (up to 10

<sup>22</sup> See a recent publication of Yu. A. Vdovin and V. M. Galitsky, Zh. Eksperim. i Teor. Fiz. **52**, 1345 (1967) [English transl.: Soviet Phys.—JETP **25**, 894 (1967)].

<sup>23</sup> F. W. Byron, N. M. McDermott, and R. Novick, Phys. Rev. **134**, A615 (1964).

<sup>24</sup> W. Happer and E. B. Saloman, Phys. Rev. **160**, 23 (1967).

<sup>25</sup> J. Meunier, A. Omont, and J. Brossel, Compt. Rend. **261**, 5033 (1965).

<sup>26</sup> A. Omont, Compt. Rend. **265**, B31 (1967).

times the natural width  $\Gamma$ ) has been obtained with the first two high-field crossings than with the different zero-field crossings (three or four times  $\Gamma$  only).

To separate self-broadening from the total experimentally measured width  $\gamma_i$ , one assumes that  $\gamma_i$  is the result of three independent relaxation processes: spontaneous emission, coherence narrowing, and resonance broadening:

$$\gamma_i = \Gamma(1 - \alpha_i x) + g_i,$$

where one expects that the resonant-broadening relaxation rate  $g_i$  is linear with respect to the perturber density  $N$ . It is well known, however, that coherence narrowing—represented by the term  $(-\Gamma\alpha_i x)$ —is linear only for low pressures:  $\alpha_i$  is a numerical coefficient smaller than 1 depending on the level and on the observable under consideration, while  $x$  varies from 0 to 1 when  $N$  grows from 0 to  $\infty$ . This explains the curvature (Fig. 7) observed when we plot the experimental width  $\gamma_i$  against  $N$ . To determine  $g_i$  from  $\gamma_i$ , one must know the value of the coherence narrowing  $\Gamma\alpha_i x$ . This is easy if the density  $N_s$  of the isotope studied is known, for relation between  $\alpha_i x$  and  $N_s$  is well known theoretically and experimentally.

From the temperature of the reservoir of the resonance cell, tables give the vapor pressure, and consequently  $N$  ( $C_s = N_s/N \sim 10^{-3}$ ). However, we do not know the exact isotopic analysis of our samples. We then estimated the isotopic concentrations by adjusting them to get a coherence-narrowing correction which leads to a straight line when one plots the corrected points versus  $N$  (Fig. 7). It must be pointed out that the values obtained in this way may differ appreciably for some of our samples from the crude estimates made during the separation of the Hg isotopes. For instance,

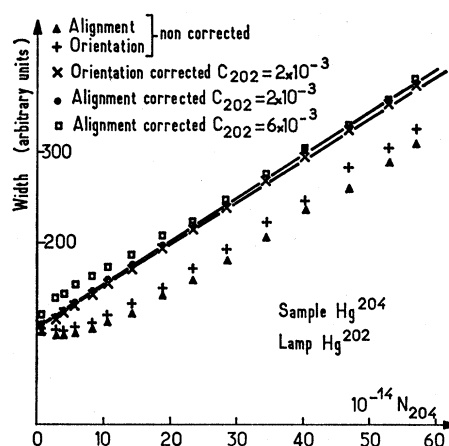


FIG. 7. Alignment and orientation broadening of Hanle effect of  $\text{Hg}^{202}$  in a vapor of concentrated  $\text{Hg}^{204}$ . The concentration of  $\text{Hg}^{202}$  is taken to be  $2 \times 10^{-3}$  in order that the points fall on a straight line after one corrects for coherence narrowing (see Sec. V B).

in Fig. 7, we have plotted corrected points, using the concentration which was given to us ( $C_2 = 6 \times 10^{-3}$ ), and clearly they are not on a straight line. We have not found a satisfactory explanation for the discrepancy, but in any case, the values of  $C_s$  do not affect very much the values of the self-broadening constants  $g_i/N$ .

The values of  $g_i/N$  for the different observables and isotopes are given in Tables II and III. Let us point out that the results given for  $\text{Hg}^{200}$  and  $\text{Hg}^{202}$  in the  $\text{Hg}^{198}$  sample do not include any coherence-narrowing correction. The concentrations  $C_{200}$  and  $C_{202}$  are so small ( $\sim 10^{-4}$ ) that coherence narrowing is still nearly linear at the pressures which we reached. Hence there is no curvature in the experimental curves, and it is not pos-

TABLE II. Measured relaxation rates of different isotopes in a very low concentration in the vapor of another concentrated isotope.  $ee\bar{g}^1(1)$  and  $ee\bar{g}^2(1)$  are, respectively, the relaxation rates of the orientation and alignment of the even isotopes;  $ee^{3/2}g^2(1)$  is the relaxation rate of the alignment of the  $F = \frac{3}{2}$  hyperfine component of  $\text{Hg}^{199}$ .

Concentrated isotope \ Observed isotope	199		200		202		
	$10^9 ee^{3/2}g^2(1)/N$	$10^9 ee\bar{g}^1(1)/N$	$10^9 ee\bar{g}^2(1)/N$	$ee\bar{g}^2(1)/ee\bar{g}^1(1)$	$10^9 ee\bar{g}^1(1)/N$	$10^9 ee\bar{g}^2(1)/N$	$ee\bar{g}^2(1)/ee\bar{g}^1(1)$
198	3.88	3.82	4.06	1.06	3.55	3.74	1.05
199	...	4.05	4.38	1.08	3.71	3.83	1.03
201	...	3.71	3.98	1.07	3.64	3.82	1.04
202	3.82	3.59	3.82	1.08	...	...	...
204	3.43	3.79	3.90	1.03	3.74	3.84	1.02

TABLE III. Comparison between theoretical and experimental values of different relaxation rates (see Sec. V C). These experimental results give, for the value of the cross section,  $ee\bar{\sigma}^2(1) = N^{-1}(v)^{-1} ee\bar{g}^2(1) = 1.46(15) \times 10^{-13} \text{ cm}^2$  for  $T = 350^\circ \text{K}$ .

		$ee\bar{g}^1(1)$	$ee\bar{g}^2(1)$	$ee^{3/2}g^2(1)$	a	b	c	$ee\bar{g}^1(1)$
Value	Theor.	3.96	4.13	4.01	3.94	3.86	3.78	3.15
( $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ )	Expt.	3.77(40)	3.98(40)	3.85(40)	4.35(40)	3.62(40)	3.40(100)	3.30(30) <sup>d</sup>
Ratio to $ee\bar{g}^2(1)$	Theor.	0.96	1	0.97				
	Expt.	0.95(3)	1	0.97(5)				

<sup>a</sup> Level crossing  $F = \frac{3}{2}, m_F = -\frac{3}{2}; F = \frac{1}{2}, m_F = \frac{1}{2}$  of  $\text{Hg}^{199}$  broadened by  $\text{Hg}^{198}$ .

<sup>b</sup> Level crossing  $F = \frac{3}{2}, m_F = -\frac{3}{2}; F = \frac{3}{2}, m_F = \frac{1}{2}$  of  $\text{Hg}^{201}$  broadened by  $\text{Hg}^{202}$ .

<sup>c</sup> Level crossing  $F = \frac{3}{2}, m_F = \frac{1}{2}; F = \frac{3}{2}, m_F = -\frac{3}{2}$  of  $\text{Hg}^{201}$  broadened by  $\text{Hg}^{202}$ .

<sup>d</sup> Measured by Perrin-Lagarde and Lennuier (Ref. 27).



sible to apply the above method to determine  $C_{200}$  and  $C_{202}$  in this sample.

### C. Comparison with Theory

We have pointed out that the theory does not predict any difference for broadening by collisions with atoms of another isotope compared with true self-broadening, as long as  $\Delta E T_c \ll 1$ , where  $\Delta E$  is the isotopic shift of the 2537 Å line and  $T_c$  the mean duration of a collision. A more precise theory (Ref. 5) leads to the following estimate: The variation of the relaxation rates of the  $6^3P_1$  level of Hg is less than 3% when  $0 < \Delta E < 17$  GHz. This includes every isotopic pair studied in zero field except the broadening of the  $F = \frac{3}{2}$  hyperfine component of  $\text{Hg}^{199}$  by  $\text{Hg}^{204}$ , in which case  $\Delta E = 22$  GHz.

Accordingly, we may neglect  $\Delta E$  for every other zero-field result, but as a precaution, we have excluded the pairs  $\text{Hg}^{202}\text{-Hg}^{199}$  and  $\text{Hg}^{202}\text{-Hg}^{201}$  in the calculation of the average of these results (we have also excluded the pairs  $\text{Hg}^{200}\text{-Hg}^{198}$  and  $\text{Hg}^{202}\text{-Hg}^{198}$ , as already mentioned in Sec. V B); accordingly, these results are an average of the results of the pairs  $\text{Hg}^{202}\text{-Hg}^{204}$ ,  $\text{Hg}^{200}\text{-Hg}^{202}$ ,  $\text{Hg}^{200}\text{-Hg}^{204}$ , and  $\text{Hg}^{200}\text{-Hg}^{199}$  for  ${}_{ee}g^k(1)$ , and of  $\text{Hg}^{199}\text{-Hg}^{198}$  and  $\text{Hg}^{199}\text{-Hg}^{202}$  for  ${}_{ee}{}^{3/2}g^2(1)$  [ ${}_{ee}{}^{3/2}g^2(1)$  is shorthand for  ${}_{ee}{}^{3/2}g_e{}^{3/2}g_e{}^{3/2}g_e{}^{3/2}g_e(1)$ ].

The values obtained in this way for the relaxation rates of alignment and orientation of even isotopes and alignment of the  $F = \frac{3}{2}$  component of  $\text{Hg}^{199}$  are given in Table III. The estimate given for the experimental uncertainty is such that every measured value falls within the error limits indicated in the table. Of course, for every isotope the relative error in the measurement of the ratio  ${}_{ee}g^2(1)/{}_{ee}g^1(1)$  is much less than the error in  ${}_{ee}g^2(1)$  or  ${}_{ee}g^1(1)$ .

The agreement with theory (Sec. III) is excellent in the zero-field case for the absolute values of  $g_i$  as well as for their ratios. The agreement is perhaps poorer, though still good, for the high-field crossings, but it should be pointed out that the zero-field values are averages of several experimental results, while each high-field value is an individual result.

Note that the broadening is smaller for the pair  $\text{Hg}^{204}\text{-Hg}^{199}$ , where  $\Delta E$  is large. The order of magnitude (10%) of the decrease of the relaxation rate is exactly that predicted by theory. However, this is also the experimental uncertainty. It is then difficult to see in this a definitive confirmation of the theory. Some new experiments with larger values of the quantity  $\Delta E T_c$  are clearly needed.

## VI. COMPARISON WITH OTHER EXPERIMENTAL RESULTS AND CONCLUSION

### A. Other Experimental Results

We would like to mention in the present section some recent precise measurements of self-broadening of op-

tical or level-crossing lines, and to compare them with theory.

*Mercury.* Perrin-Lagarde and Lennuier<sup>27</sup> have studied self-broadening of the 2537 Å absorption line, using magnetic scanning. This technique allows measurements at low pressures where the impact theory is valid. The results on the broadening of  $\text{Hg}^{198}$  by collisions with  $\text{Hg}^{198}$  and of  $\text{Hg}^{196}$  by collisions with the other isotopes of natural mercury are in excellent agreement with theory (see Table III). Let us point out that the relaxation rate  ${}_{ee}g^1(1)$  is much less than  ${}_{ee}g^2(1)$  or  ${}_{ee}g^1(1)$  because the atomic ground state is not perturbed by resonant collisions.

*Helium and neon.* Self-broadening of several emission lines resulting from transitions from an upper excited level to the resonance level has been measured by Kuhn and Vaughan,<sup>28</sup> using a high-resolution spectrometer. The slope of the straight line obtained for the variation of the experimental width with  $N$  is in very good agreement with theory. But there is a large discrepancy between the values of the natural width given by theory and the extrapolation to  $N=0$  of this straight line. We do not know any fully satisfactory explanation of this feature.

*Lead.* As we mentioned in Sec. V A, because of the possibility of decay of  $(6s^26p7s) {}^3P_1^0$  resonance state of Pb to low-populated metastable levels, observation of self-broadening of zero-field level crossing is relatively easy,<sup>24</sup> and Happer and Saloman succeeded in performing measurements in a fairly high range of pressures. In this experiment they measured  ${}_{ee}g^2(1+2)$  and  ${}_{ee}g^1(1+2)$ ; their results are<sup>29</sup>

$$\begin{aligned} {}_{ee}K^2(1+2) &= 3.2 \pm 0.7, \\ {}_{ee}K^1(1+2)/{}_{ee}K^2(1+2) &= {}_{ee}g^1(1+2)/{}_{ee}g^2(1+2) \\ &= 1.21 \pm 0.05, \end{aligned}$$

which is in good agreement with our theoretical values (2.63 and 1.20; see Table I).

### B. Concluding Remarks

We have demonstrated the usefulness of an irreducible representation in Liouville space for the density matrix. It makes possible a compact and very complete calculation of every relaxation rate of the problem.

The precise numerical calculation performed here of these relaxation rates allows a significant comparison with the very accurate experimental results obtained with mercury and reported in Sec. V. Using a mixture of two isotopes allows the observation of self-broadening of level-crossing and double-resonance lines without the spurious effects due to imprisonment of resonance radia-

<sup>27</sup> D. Lagarde and R. Lennuier, *Compt. Rend.* **261**, 919 (1965); D. Perrin-Lagarde, *ibid.* **263**, B1384 (1966).

<sup>28</sup> J. M. Vaughan, *Proc. Phys. Soc. (London)* **A295**, 164 (1966).

<sup>29</sup> This estimated error is not explicitly given by Happer and Saloman. We crudely deduced it from their plotted experimental uncertainties (Ref. 24, Fig. 8).

tion. One may think, of course, of extending this method to other elements in a large number of similar cases.

We feel that the most striking conclusion of the features reported here is the very good agreement between theory and experiment. This leads us to believe that one may trust the theory for other similar cases. Some problems remain unsolved in a precise calculation of self-broadening of optical-resonance lines. They are related in some way to transfer of "optical coherence," "super-

radiance," multiple scattering of resonance radiation, etc., but we do not think that they can lead to the discovery of very important new phenomena.

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### *N*-Representability Problem for an Odd Number of Fermions\*

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The *N*-representability problem for the first- and second-order density matrices is considered when *N* is an odd integer. Attention is restricted to those density matrices derivable from functions whose natural spin orbitals have certain paired properties. Neither pairing of spatial orbitals nor special spin properties are required in general, but they are discussed as special cases. New sufficient conditions for *N*-representability of the first-order density matrix are given. The second-order density matrix is studied in detail. Special cases in which the *N*-representability problem for the second-order density matrix can be solved are considered.

#### I. INTRODUCTION

ATTEMPTS to describe many-particle systems by calculating the wave function have had only limited success. This is primarily due to the computational problems involved in calculating a many-particle wave function variationally. Since the second-order density matrix is a function of the position and spin of only four particles, it should be easier to work with than an *N*-particle wave function. Therefore, there has been considerable interest recently in studying the first- and second-order density matrices for many-particle systems.

The expectation value of any physical property which depends on only one or two particles can be calculated if one knows the second-order density matrix.<sup>1,2</sup> Thus one can obtain a satisfactory description of the system from the second-order density matrix, without knowing the wave function. In fact, the first- and second-order density matrices generally give a more meaningful description of the system than a complicated wave function.<sup>2-11</sup> Therefore, one might hope to determine the

second-order density matrix directly, without first finding the wave function. However, in order to apply a valid variational principle to the second-order density matrix, one must first, at least partially, solve the *N*-representability problem.<sup>12,13</sup> For fermion systems, this is the problem of determining the necessary and sufficient conditions on a density matrix which guarantee that it can be derived from an antisymmetric *N*-particle wave function.

This paper is concerned with the *N* representability of both the first- and second-order density matrices for systems containing an odd number of fermions. Since our aim is to eventually describe physical systems through their density matrices alone, we are not necessarily interested in finding a completely general mathematical solution which may be computationally intractable. Instead, we hope that by confining our attention to those density matrices derivable from a restricted but physically realistic class of functions, we may find a useful partial solution. Therefore, we will restrict ourselves to those density matrices derived from functions

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<sup>1</sup> P. O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).

<sup>2</sup> R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960).

<sup>3</sup> R. McWeeny, *Proc. Roy. Soc. (London)* **A253**, 242 (1959).

<sup>4</sup> G. P. Barnett and H. Shull, *Phys. Rev.* **153**, 61 (1967).

<sup>5</sup> P. O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1956).

<sup>6</sup> G. P. Barnett, J. Linderberg, and H. Shull, *J. Chem. Phys.* **43**, S80 (1965).

<sup>7</sup> D. W. Smith and S. J. Fogel, *J. Chem. Phys.* **43**, S91 (1965).

<sup>8</sup> J. E. Harriman, *J. Chem. Phys.* **40**, 2827 (1964).

<sup>9</sup> A. Hardisson and J. E. Harriman, *J. Chem. Phys.* **46**, 3639 (1967).

<sup>10</sup> R. McWeeny and Y. Mizuno, *Proc. Roy. Soc. (London)* **A259**, 554 (1961).

<sup>11</sup> References 2-10 are intended to be representative rather than complete.

<sup>12</sup> R. H. Tredgold, *Phys. Rev.* **105**, 1421 (1957).

<sup>13</sup> Y. Mizuno and T. Izuyama, *Progr. Theoret. Phys. (Kyoto)* **18**, 33 (1957).