Collision-Induced Anisotropic Relaxation in Gases

C. H. Wang and W. J. Tomlinson
Bell Telephone Laboratories, Holmdel, New Jersey 07733
(Received 6 January 1969)

An expression is derived for the cross sections, $\sigma_j^{(x)}$, for the collision-induced relaxation of the multipole moments of an ensemble of excited atoms in a state of total angular momentum j. Various general sum rules are obtained for the $\sigma_j^{(x)}$, as well as for the $\Lambda_j^{(x)} \equiv \sigma_j^{(x)} - \sigma_j^{(0)}$, the cross sections for reorienting collisions. For a $j=1$ state, one obtains $\Lambda_1^{(1)}/\Lambda_1^{(2)} = \frac{5}{3}$. This result implies that the cross section for collision induced $|\Delta m| = 2$ transitions is always twice that for $|\Delta m| = 1$ transitions, independent of the assumed interaction potential. Absolute cross sections are obtained using the van der Waals collision model. Translational motion is treated in a classical linear path approximation. It is shown that the cross sections can be written in the form $\sigma_j^{(x)} = D\phi_j^{(x)}\langle v^{3/5}\rangle / \langle v\rangle$, where v is the relative velocity between the colliding atoms, D depends on the particular atoms and states considered, and $\phi_j^{(x)}$ is a geometric factor which is tabulated for j values up to $j=8$. The $\Lambda_j^{(x)}$ are related to the cross sections for transfers between magnetic sublevels. It is shown that in the present model a transfer from sublevel α to $-\alpha$ is forbidden for states with half-integer j values.

I. INTRODUCTION

Atomic collisions causing reorientations of the angular momentum of an atom are important relaxation processes in understanding the experiments of double resonance and Hanle effect,[1] line shapes for scattering and absorbing of radiation,[2] and nuclear spin relaxation.[3] (We use the word "atom" even though the discussion given in this paper applies to molecules equally well.) Recently, it has also been shown that reorienting collisions are responsible for the "strong coupling" of the two circular polarizations of the 1.52-μ Ne transition of the He-Ne laser.[4,5]

The collision cross sections for mixing of the Zeeman sublevels (or reorientation of the angular momentum vector) caused by resonant collisions were calculated numerically by D'yakanov and Perel'[6] for the case of a $j=1$ state colliding with a ground-state atom of $j=0$. Generalizing the theory of resonant and nonresonant collisions of Byron and Foley,[7] Omont[8] has derived a general expression for the cross sections for the relaxations of the multipole moments, $\sigma_j^{(x)}$ (to be defined in Sec. II). He also worked out explicitly the $j=1$ case. However, no general method has previously been given for calculating the cross sections for states of arbitrary angular momentum.

In this paper we give a method for calculating these cross sections. We first derive, in Sec. II, a general formula for the cross sections in the spherical tensor representation. In Sec. III we obtain general sum rules for $\sigma_j^{(x)}$. Finally, in Sec. IV the calculation is specialized to the case of van der Waals collisions (or nonresonant collisions). We then develop an algorithm for calculating cross sections for a state with arbitrary total angular momentum j.

II. GENERAL FORMULA

At low densities the time rate of change of the density operator $\rho(t)$ describing an atom, in a state of total angular momentum j, due to uncorrelated binary collisions can be written as

$$\frac{\partial\rho(t)}{\partial t} = -2\pi\sum_i n_i \int d^3v_i\, |\vec{v}_i| \times f(\vec{v}_i) b_i\, db_i \langle \Delta_i \rho(t)\rangle_{\rm av}, \tag{1}$$

where b_i is the impact parameter corresponding to the collision of the specifically considered atom with a perturbing atom of the ith kind; $\vec{v}_i$ is their relative velocity, $f(\vec{v}_i)$ is the relative velocity distribution of the perturber, and n_i is its number density. The $\langle\cdots\rangle_{\rm av}$ indicates the angular average of all the collisions at different angles. Here $\Delta_i\rho$ is given by

$$\Delta_i\rho(t) = \rho(t) - \langle u_i | S_i | \mu_i\rangle \rho(t) \langle \mu_i | S_i^{+} | \mu_i\rangle, \tag{2}$$

where the collision operator $S_i(t, t_0)$ satisfies the operator equation

$$\partial S_i(t, t_0)/\partial t = -iS_i(t, t_0) V_i(t) \tag{3}$$

with the initial condition given by

$$S_i(t_0, t_0) = 1.$$

The operator $V_i(t)$ is given by

$$V_i(t) = e^{-iH_2 t} U_i(t) e^{iH_2 t},$$

where H_2 is the unperturbed Hamiltonian of two colliding atoms, and $U_i(t)$ is the interaction potential acting between atoms during the collision. The time dependence in $U_i(t)$ is due to the translational motion of the atoms.

In writing Eq. (1), we assume that the perturbing atom is initially in the ground state $|\mu_i\rangle$ described by a relative velocity distribution $f(\vec{v}_i)$. The density operator $\rho(t)$ in Eq. (1) is obtained by making a *Stosszahlansatz*, namely, one replaces $\rho(t_0)$ by $\rho(t)$ where t_0 is the time when a collision event takes place. This assumption is justifiable only if $\Delta t = t - t_0$ is short such that the density operator $\rho(t)$ does not change significantly in Δt.

Since we are interested only with m_j mixing collisions, the specific density matrix for this purpose is obtained from Eq. (1) as

$$\frac{\partial}{\partial t}\{\rho_{j_\alpha j_\beta}(t)\} = -2\pi\sum_i n_i \int d^3 v_i |\vec{v}_i| f(\vec{v}_i) \times b_i db_i \sum_{\gamma\delta} \langle \Gamma_i(j|\alpha\beta;\gamma\delta)\rangle_{\rm av} \rho_{j_\gamma j_\delta}(t), \tag{4}$$

where the four index matrix (tetradic) is given by

$$\langle \Gamma_i(j|\alpha\beta;\gamma\delta)\rangle_{\rm av} = \langle \delta_{\alpha\gamma}\delta_{\beta\delta} - \langle j_\alpha \mu_i | S_i | j_\gamma \mu_i\rangle \langle j_\delta \mu_i | S_i^+ | j_\beta \mu_i\rangle\rangle_{\rm av}. \tag{5}$$

Here we have labeled the angular momentum of a state by the letter j and its projection along the quantization axis by a subscript. Other quantum numbers are not explicitly specified.

To evaluate Eq. (5), we express the interaction potential $U_i(t)$ in a coordinate system fixed in the collision plane, i.e., the plane of the impact parameter $\vec{b}_i$ and the relative velocity $\vec{v}_i$. We then rotate the state vectors to this new coordinate frame with the help of rotation matrices. Therefore Eq. (5) becomes

$$\langle \Gamma_i(j|\alpha\beta;\gamma\delta)\rangle_{\rm av} = \sum_{lmpq} \langle D_{\alpha l}^{(j)} D_{\gamma m}^{*(j)} D_{\delta p}^{(j)} D_{\beta q}^{*(j)}\rangle_{\rm av} \times (\delta_{lm}\delta_{pq} - \langle j_l \mu_i | S_i | j_m \mu_i\rangle \times \langle j_p \mu_i | S_i^+ | j_q \mu_i\rangle). \tag{6}$$

The angular average can be carried out by first expressing the four rotation matrices in terms of two rotation matrices by means of the Clebsch-Gordan series,[9] and then performing the angular integration with the help of the orthogonality property of the D matrices. The final result is

$$\langle \Gamma_i(j|\alpha\beta;\gamma\delta)\rangle_{\rm av} = \sum_{J,n} \begin{pmatrix} j & j & J \\ \alpha & \delta & n \end{pmatrix} \begin{pmatrix} j & j & J \\ \gamma & \beta & n \end{pmatrix} G_i(J), \tag{7}$$

where $G_i(J)$ is given by

$$G_i(J) = \sum_{lmpqn'} (2J+1) \begin{pmatrix} j & j & J \\ l & p & n' \end{pmatrix} \begin{pmatrix} j & j & J \\ m & q & n' \end{pmatrix} \times (\delta_{lm}\delta_{pq} - \langle j_l \mu_i | S_i | j_m \mu_i\rangle \times \langle j_p \mu_i | S_i^+ | j_p \mu_i\rangle), \tag{8}$$

and the quantity within the curved bracket is the Wigner 3-j symbol.[9]

We see from Eqs. (4) and (7) that the decay of

$$\rho_{j_\alpha j_\beta}$$

is anisotropic; therefore it is convenient to expand the density matrix in a representation such that the equations are decoupled. This expansion can be accomplished by the following transformation[9]:

$$\rho_{j_\alpha j_\beta} = \sum_{xq} \rho_q^{(x)} [T_{-q}^{(x)}]_{j_\alpha j_\beta}, \tag{9}$$

where $\rho_q^{(x)}$ is a c number, and $T_q^{(x)}$ is an irreducible tensor operator of rank x with matrix element normalized to

$$[T_{\pm q}^{(x)}]_{j_\alpha j_\beta} = (-1)^{j-\alpha\pm q}(2x+1)^{1/2} \begin{pmatrix} j & x & j \\ -\alpha & \pm q & \beta \end{pmatrix}.$$

The expansion in terms of the $\rho_q^{(x)}$ has direct physical meanings. For example, $\rho_0^{(0)}$ is simply the population of atoms in the state $|j\rangle$; $\rho_q^{(1)}$ is proportional to the qth component of the total angular momentum (or magnetic moment) of the ensemble of the atoms in the state $|j\rangle$. In short, $\rho_q^{(x)}$ is proportional to the qth component of the 2^x-pole moment of an ensemble of atoms in the state $|j\rangle$. (The range of x is from 0 to $2j$.)

Substituting Eq. (7) into (4) and performing the transformation to the spherical tensor basis described by Eq. (8), we obtain the result

$$\frac{\partial}{\partial t}\rho_q^{(x)} = -\gamma_j^{(x)} \rho_q^{(x)}, \tag{10}$$

where

$$\gamma_j^{(x)} = 2\pi\sum_i n_i \int d^3 v_i |\vec{v}_i| f(\vec{v}_i)$$

$$\times b_i db_i \sum_J G_i(J) \begin{Bmatrix} x & j & j \\ J & j & j \end{Bmatrix} \tag{11a}$$

or $$\gamma_j^{(x)} = 2\pi \sum_i n_i \int d^3 v_i b_i db_i |\vec{v}_i|$$

$$\times f(\vec{v}_i) \sigma_j^{(x)}(b_i v_i), \tag{11b}$$

and the quantity in the curly bracket is the Wigner 6-j symbol.[9] The cross section $\sigma_j(x)(b_i v_i)$ is given by

$$\sigma_j^{(x)}(b_i v_i) = \sum_J G_i(J) \begin{Bmatrix} x & j & j \\ J & j & j \end{Bmatrix} . \tag{12}$$

The expression for the cross section given by Omont[8] [cf. Eq. (32) of Ref. 8] can be derived from Eq. (12) by first expanding further the S matrices appearing in $G_i(J)$ [cf. Eq. (8)] in the spherical tensor representation and then making use of the properties of 6-j symbols. However, for analytical or numerical calculations of the cross sections, for a state with an arbitrary angular momentum, it is more convenient to use the form given in Eq. (12) because the symmetry property of the S matrix in the "lm" representation eliminates large efforts in the calculation, as will be seen below.

III. SUM RULES FOR $\sigma_j^{(x)}(b_i v_i)$

It is convenient to introduce a scattering T matrix which is related to the S matrix by

$$\langle j_l \mu_i | S_i | j_m \mu_i \rangle = \delta_{lm} + T_{lm} \tag{13}$$

and $$\langle j_p \mu_i | S_i^+ | j_q \mu_i \rangle = \delta_{pq} + T^*_{pq} .$$

Substituting Eq. (13) into Eq. (8), one obtains

$$G_i(J) = -(2J+1)\left[\frac{1}{2j+1}\sum_p (T_{pp} + T^*_{pp}) - \sum_{lmpqn'} \begin{pmatrix} j & j & J \\ l & p & n' \end{pmatrix} \begin{pmatrix} j & j & J \\ m & q & n' \end{pmatrix} T_{lm} T^*_{pq}\right] . \tag{14}$$

It follows from Eqs. (12) and (14) that

$$\sigma_j^{(0)} = \frac{-1}{2j+1} \sum_\alpha [(T_{\alpha\alpha} + T^*_{\alpha\alpha}) + \sum_\beta T_{\alpha\beta} T^*_{\beta\alpha}], \tag{15}$$

where, for brevity, we have not written out the arguments of the cross section.

By contracting the index x in Eq. (12), one obtains readily the following sum rules for $\sigma_j(x)$:

(a) $$\sum_{x=0}^{2j} (2x+1)\sigma_j^{(x)}$$

$$= -(2j+1)\sum_\alpha (T_{\alpha\alpha} + T^*_{\alpha\alpha}) - \left(\sum_\alpha T_{\alpha\alpha}\right)\left(\sum_\alpha T^*_{\alpha\alpha}\right), \tag{16}$$

(b) $$\sum_{x=0}^{2j} (-1)^{x+2j} (2x+1)\sigma_j^{(x)}$$

$$= -\sum_\alpha [(T_{\alpha\alpha} + T^*_{\alpha\alpha}) + \sum_\beta (-1)^{2j+\alpha+\beta} T_{\alpha\beta} T^*_{-\alpha-\beta}] . \tag{17}$$

If we consider the special case where the condition

$$T_{-\alpha-\beta} = (-1)^{2j-\alpha-\beta} T_{\beta\alpha} \tag{18}$$

is satisfied, the sum rule (b) reduces immediately to

(b′) $$\sum_{x=0}^{2j} (-1)^{2j+x} (2x+1)\sigma_j^{(x)} = (2j+1)\sigma_j^{(0)} . \tag{19}$$

From symmetry arguments, one intuitively expects that the condition expressed in Eq. (18) is satisfied by many physical systems. We shall see in the next section that the van der Waals potential model satisfies this condition.

The sum rule (b′) can be simplified further if one realizes that the relaxation of the multipole moments are from two contributions: (1) excitation transfer from the atom under consideration to perturbers, and (2) the m_j mixing among Zeeman sublevels. These two processes give independent contributions to $\sigma_j^{(x)}$; therefore one can write

$$\sigma_j^{(x)} = \Lambda_j^{(x)} + \sigma_j^{(0)} , \tag{20}$$

where the cross section $\Lambda_j^{(x)}$ accounts only for the collisions which mix up the Zeeman sublevels, and $\sigma_j^{(0)}$ accounts for the transfer of population.

Substituting Eq. (20) into Eq. (19), one obtains a simple sum rule for $\Lambda_j^{(x)}$ as

$$\sum_{x=2,4,\ldots} (2x+1)\Lambda_j^{(x)} = \sum_{x=1,3,\ldots} (2x+1)\Lambda_j^{(x)} . \tag{21}$$

Except for the conditions given in Eq. (18), this result is independent of any specific form of the interaction potential. The general validity of Eq. (21), therefore, provides a convenient check in computing reorienting cross sections resulting from any specific interaction.

The case $j=1$ is of considerable interest because it corresponds to many experiment situations. One obtains immediately from Eq. (21) that

$$\Lambda_1^{(1)}/\Lambda_1^{(2)}=\tfrac{5}{3}\ . \tag{22}$$

We show in Appendix I that this ratio implies that the cross section for collision-induced $|\Delta m|=2$ transitions is twice the cross section for $|\Delta m|=1$ transitions. Coupling this $\frac{5}{3}$ ratio with the experimentally measured critical magnetic field and the spontaneous decay rates in the 1.52-μ He-Ne laser line, we have determined the anistropic relaxation cross sections for the $2s_2$ state ($j=1$) of the Ne atom in a He-Ne laser discharge.[5]

IV. VAN DER WAALS COLLISIONS WITH AN r_i^{-6} TYPE POTENTIAL

The calculation of the T matrix based on the van der Waals interaction potential model will be of the central attention in this section. The equation of motion for the S matrix can be obtained from Eq. (3) by taking the required matrix element as

$$i\langle j_l\mu_i|\dot{S}_i|j_m\mu_i\rangle=\sum_{pq_i}\langle j_l\mu_i|S_i|pq_i\rangle \times\langle pq_i|U_i(t)|j_m\mu_i\rangle\exp[it(E_{pq_i}-E_{j_m\mu_i})]. \tag{23}$$

A similar equation applies to $\langle j_p\mu_i|S_i^{+}|j_q\mu_i\rangle$.

For the collision of two neutral atoms, the interaction potential can be expressed in terms of a multipole expansion containing dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, etc., interactions provided that the two atoms are far apart. In general, there is also a hard-core interaction which becomes important when the electron clouds of two atoms begin to overlap. The repulsive hard-core interaction is presumably unimportant in treating the anisotropy of the relaxation rate because as this interaction becomes operative the atomic state is drastically changed and there will be little correlation between the state of the atom before and after the impact, thus the decay caused by these collisions is expected to be isotropic. [Furthermore, the cross section due to the hard-core interaction is small ($\leq 10^{-17}$ cm^2).[10]] We therefore neglect the hard-core interaction and take $U_i(t)$ to be the dipole-dipole interaction for the subsequent calculations.

Therefore in the classical path approximation for the translational motion, one writes

$$U_i(t)=\frac{\vec{P}\cdot\vec{P}_i}{r_i^{3}(t)}-3\frac{[\vec{P}\cdot\vec{r}_i(t)][\vec{P}_i\cdot\vec{r}_i(t)]}{r_i^{5}(t)}\ , \tag{24}$$

where in the collision coordinate system $r_i(t)$ is given by

$$r_i(t)=|\vec{b}_i+\int_0^t\vec{v}_i(t')\,dt'|\simeq(b_i^{2}+v_i^{2}t^{2})^{1/2}.$$

The last equality is the result of the linear-path approximation. In the case of states with energy satisfying

$$\Delta E_i\equiv E_{pq_i}-E_{m\mu_i}\ll 1/\tau_c, \tag{25}$$

where τ_c is the average duration of collision, the phase factor in Eq. (23) can be set equal to unity and one has the condition for the "sudden approximation." The S matrix can then be approximated to be[11]

$$\langle j_l\mu_i|S_i|j_m\mu_i\rangle=\langle j_l\mu_i|e^{-iQ_i}|j_m\mu_i\rangle, \tag{26}$$

where

$$Q_i=\int_{-\infty}^{\infty}dt\,U_i(t)\simeq\frac{2}{b_i^{2}v_i}(P_xP_{ix}-P_zP_{iz}), \tag{27}$$

provided that one includes only states which are connected by the operator Q_i and have energies such that Eq. (25) is satisfied. [This case is also known as the resonant collision. The coordinate system used in Eq. (27) has the x, y, and z axes in the directions $\vec{v}_i\times\vec{b}_i$, $\vec{v}_i$, and $\vec{b}_i$, respectively.] On the other hand, if the condition

$$\Delta E_i\equiv E_{pq_i}-E_{m\mu_i}\gg 1/\tau_c \tag{28}$$

is satisfied, one can use the "adiabatic approximation" and the S matrix can be approximated to be[11]

$$\langle j_l\mu_i|S_i|j_m\mu_i\rangle=\langle j_l|e^{-iW_i}|j_m\rangle, \tag{29}$$

where W_i is the effective potential for van der Waals collisions given by

$$\begin{aligned}W_i&=\langle\Delta E_i\rangle^{-1}\int_{-\infty}^{\infty}\langle\mu_i|U_i^{2}(t)|\mu_i\rangle dt\\&\simeq[4(\pi)^{3/2}p_i^{2}p^{2}/16\langle\Delta E_i\rangle v_i b_i^{5}]\\&\quad\times\{2Y_{00}(\theta,\phi)+\tfrac{3}{2}(\tfrac{1}{5})^{1/2}Y_{20}(\theta,\phi)\\&\quad-\tfrac{1}{4}(\tfrac{2}{15})^{1/2}[Y_{22}(\theta,\phi)+Y_{2-2}(\theta,\phi)]\},\end{aligned} \tag{30}$$

where $p_i^{2}=\langle\mu_i|P_i^{2}|\mu_i\rangle$ and θ and ϕ are the polar and azimuthal angle of $\vec{p}=e\vec{r}$ with respect to the coordinate system $(\vec{b}\times\vec{v}_i,\vec{v}_i,\vec{b}_i)$. The term Y_{00} cannot contribute to the cross section because it only perturbs the Zeeman sublevels of the state with equal shifts in energy. It can therefore be ignored in the calculation of S matrix. The quantity $\langle\Delta E_i\rangle$, the average of ΔE_i, is the result of

the closure approximation used in deriving Eq. (29), and it can be estimated from the energy-level diagram if the information about oscillator strengths of the state $|j\rangle$ is available. [The case described by Eq. (29) is also known as the non-resonant collision.]

For the (electric) dipole-dipole interaction model, the resonant collision is possible only when the angular momenta of the colliding pair of atoms satisfy $|\Delta j| = 0, 1$. Quite often the perturbing atom is in a ground state of zero angular momentum, and in order for the dipole-dipole interaction potential to be an important mechanism the other atom must be in a state with $j = 1$. This is the case in the He-Ne laser oscillating on the 1.52, 1.15, or 0.633 μ, etc., transitions, but the collision cross section is not particularly large, so that resonant m_j mixing collisions are presumably insignificant in He-Ne gas lasers because of the low Ne/He density ratio in the system. However, if allowed by the dipole-dipole selection rule, the resonant collision can be one of the important mechanisms contributing to the decay of *population* in a laser due to the small probability of collisions between an active atom and an identical ground-state atom having a similar z component of velocity. Only the active atoms in a small region of the Doppler profile contribute to the intensity of a single-mode laser. The resonant collisions we considered here are the type of collisions in which the atoms exchange excitation but do not significantly alter their velocities. Therefore a collision between two atoms of the same kind is more likely to annihilate the excited atom of "right" velocity and to create a new active atom elsewhere in the velocity distribution. The excitation of the atom contributing to the laser intensity is then lost. This case is quite different from experiments using the Hanle effect, where resonant collisions cannot contribute to $\sigma_j^{(0)}$ because there the atoms of every velocity class contribute to the depolarization of electromagnetic radiation. The calculation of the cross section for multipole moment relaxation by resonant collisions for the case of the Ne $2s_2$ state is given in Ref. 5; for other cases the method developed below can be used equally well and we will not consider it in this paper.

We now consider the van der Waals collision calculation. With the help of the Wigner-Eckart theorem,[9] the matrix element for the operator W is easily found, for integer j, as

$$\langle j_l | W_i | j_m \rangle = W_{lm}(j) = (-1)^l A_i (2j+1) \times \begin{pmatrix} j & 2 & j \\ 0 & 0 & 0 \end{pmatrix} \left\{ 3 \begin{pmatrix} j & 2 & j \\ -l & 0 & m \end{pmatrix} - (\tfrac{1}{6})^{1/2} \left[\begin{pmatrix} j & 2 & j \\ -l & 2 & m \end{pmatrix} + \begin{pmatrix} j & 2 & j \\ -l & -2 & m \end{pmatrix} \right] \right\} \quad (31)$$

and, for half-integer j, as

$$\langle j_l | W_i | j_m \rangle = -(-1)^{l-\frac{1}{2}} A_i [(2j+4)(2j-1)]^{\frac{1}{2}} \times \begin{pmatrix} 2 & j+\frac{1}{2} & j+\frac{1}{2} \\ 0 & 0 & 0 \end{pmatrix} \left\{ 3 \begin{pmatrix} j & 2 & j \\ -l & 0 & m \end{pmatrix} - (\tfrac{1}{6})^{1/2} \left[\begin{pmatrix} j & 2 & j \\ -l & 2 & m \end{pmatrix} + \begin{pmatrix} j & 2 & j \\ -l & -2 & m \end{pmatrix} \right] \right\}, \quad (32)$$

where

$$A_i = \pi p^2 p_i^{\,2} / 16 \langle \Delta E_i \rangle b_i^{\,5} v_i .$$

The properties of the 3-j symbol give immediately that the nonzero elements in the matrix $W_{lm}(j)$ are those with $|l-m| = 2, 0$, and that W is a symmetric square matrix. Therefore the eigenvalues of $W_{lm}(j)$ are real.

If we make the power series expansion of the operator e^{-iW} in the form

$$e^{-iW} = \sum_n [(-1)^n / n!] W^n, \quad (33)$$

then the crux of the calculation lies in the reduction of the matrix W^n. According to the Hamilton-Cayley theorem[12] any symmetric square matrix satisfies the equation

$$\Pi_i (\lambda_i I - W) = 0, \quad (34)$$

where the λ_i are the eigenvalues of W, and the product goes over all distinct eigenvalues. From Eq. (34) it follows that W^n can be reduced to contain powers of W only up through one less than the number of its distinct eigenvalues. Also, from Eq. (34), one can show that, for distinct eigenvalues, the set of operators

$$Z_i = \prod_{l \neq i} (\lambda_l I - W)/(\lambda_l - \lambda_i)$$

form a complete set of projectors into the eigenvalues of W. Hence

$$Z_i Z_j = Z_i \delta_{ij}, \text{ and } W = \sum_j \lambda_j Z_j, \quad (35)$$

so that $W^n = \sum_j \lambda_j^{\,n} Z_j$, and $e^{-iW} = \sum_j e^{-i\lambda_j} Z_j$. (36)

The reduction of W^n in terms of projectors Z_i's is the reduced form of Sylvester's theorem.[12] From Eqs. (13), (29), and (36) it then follows that

$$T_{lm} = \sum_j (e^{-i\lambda_j} - 1)(Z_j)_{lm} . \quad (37)$$

Substituting Eq. (37) into Eq. (14), we obtain

$$G_i(J) = (2J+1) \left[\frac{4}{2J+1} \sum_a d_a \sin^2(\lambda_a/2) \right.$$

$$-2\sum_{lmpqn'}\begin{pmatrix} j & j & J \\ l & p & n' \end{pmatrix}\begin{pmatrix} j & j & J \\ m & q & n' \end{pmatrix} \times \sum_{a=1}^{2j+1}\sum_{b=1}^{2j+1}(Z_a)_{lm}(Z_b)_{pq} \times\left[\sin^2\tfrac{1}{2}\lambda_a+\sin^2\tfrac{1}{2}\lambda_b-\sin^2\tfrac{1}{2}(\lambda_a-\lambda_b)\right]. \quad (38)$$

To obtain Eq. (38) we have used the identity

$$\mathrm{Tr}Z_a = d_a,$$

where d_a is the number of degenerate eigenvalues corresponding to λ_a. The cross section $\sigma_j^{(x)}(b_i v_i)$ is then

$$\sigma_j^{(x)}(b_i v_i)=\frac{4}{2j+1}\sum_a d_a \sin^2(\lambda_a/2) - 2\sum_{Jn'}\sum_{lmpq}(2J+1)\begin{pmatrix} j & j & J \\ l & p & n' \end{pmatrix}\begin{pmatrix} j & j & J \\ m & q & n' \end{pmatrix} \times\begin{Bmatrix} j & j & x \\ j & j & J \end{Bmatrix}\sum_{q=1}^{2j+1}\sum_{b=1}^{2j+1}(Z_a)_{lm}(Z_b)_{pq} \times\left[\sin^2\tfrac{1}{2}\lambda_a+\sin^2\tfrac{1}{2}\lambda_b-\sin^2\tfrac{1}{2}(\lambda_a-\lambda_b)\right]. \quad (39)$$

By means of the properties of the j symbols and the projection operators, one obtains from Eqs. (15) and (19)

$$\sigma_j^{(0)}=\sum_x(-1)^x(2x+1)\sigma_j^{(x)}=0. \quad (40)$$

This is because the effective potential W_i used for van der Waals collisions is of even parity and cannot change the population.

The substitution of Eq. (37) into Eq. (16) gives

$$\sum_x^{2j+1}(2x+1)\sigma_j^{(x)}=\sum_{x=1}^{2j+1}(2x+1)\Lambda_j^{(x)} = \sum_{a=1}^{2j+1}\sum_{b=1}^{2j+1} d_a d_b \sin^2\tfrac{1}{2}(\lambda_a-\lambda_b). \quad (41)$$

For $j=1$, one has

$$3\Lambda_1^{(1)}+5\Lambda_1^{(2)}=4[\sin^2\tfrac{1}{2}(\lambda_1-\lambda_2) +\sin^2\tfrac{1}{2}(\lambda_1-\lambda_3)+\sin^2\tfrac{1}{2}(\lambda_2-\lambda_3)]. \quad (42)$$

One readily shows from Eq. (31) that the eigenvalues of the W_{lm} (1) matrix are

$$\lambda_1=\frac{6B_i}{5b_i^5},\quad \lambda_2=\frac{-4B_i}{5b_i^5},\quad \text{and}\quad \lambda_3=\frac{-2B_i}{5b_i^5}$$

where $B_i=b_i^5A_i$.

Using the $\frac{5}{3}$ ratio for $\Lambda_1^{(1)}/\Lambda_1^{(2)}$, we obtain from Eq. (42)

$$\Lambda_1^{(1)}=\tfrac{5}{3}\Lambda_1^{(2)}=\tfrac{2}{3}[\sin^2(B_i/5b_i^5) +\sin^2(4B_i/5b_i^5)+\sin^2(B_i/b_i^5)]. \quad (43)$$

This result agrees with that of Omont[8] for the $j=1$ case.

It is now possible to develop an algorithm for calculating the cross sections for a state with arbitrary j.

If one defines a matrix $X_{lm}(j)$ which is related to the $W_{lm}(j)$ given in Eqs. (31) and (32) by

$$W_{lm}(j)=B_i X_{lm}(j) \quad (44)$$

where $$B_i=A_i b_i^5=\frac{\pi p^2 p_i^2}{16\langle\Delta E_i\rangle v_i},$$

then the eigenvalues of the $X_{lm}(j)$ matrix δ_1, δ_2, ..., and δ_{2j+1} are related to λ_1, λ_2, ..., λ_{2j+1} [the eigenvalues of the $W_{lm}(j)$ matrix] by

$$\lambda_a=\delta_a/b_i^5,\quad \text{with}\quad a=1,2,\ldots,2j+1. \quad (45)$$

The projector Z_i remains unchanged.

Rewriting the T matrices given in Eq. (37) in terms of δ_a and then substituting them into Eqs. (38) and (12) and carrying out the b_i and the v_i integrations, we obtain the cross section due to the ith perturber at all impact parameters as the following:

$$\sigma_j^{(x)}(i)=\Lambda_j^{(x)}(i)\equiv\gamma_j^{(x)}(i)/n_i\langle v_i\rangle = D_i\frac{\pi^2}{4}\frac{\csc\frac{1}{5}\pi}{\Gamma(\frac{2}{5})}\frac{\langle v_i^{3/5}\rangle}{\langle v_i\rangle}\left[\frac{4}{2j+1}\sum_a\delta_a^{2/5}d_a - 2\sum_{Jn'}\sum_{lmpq}(2J+1)\begin{pmatrix} j & j & J \\ l & p & n' \end{pmatrix}\begin{pmatrix} j & j & J \\ m & q & n' \end{pmatrix} \times\begin{Bmatrix} x & j & j \\ J & j & j \end{Bmatrix}\sum_{a=1}^{2j+1}\sum_{b=1}^{2j+1}(Z_a)_{lm}(Z_b)_{pq} \times[\delta_a^{2/5}+\delta_b^{2/5}-(\delta_a-\delta_b)^{2/5}]\right], \quad (46)$$

where $D_i=(\pi p^2 p_i^2/16\langle\Delta E_i\rangle)^{2/5}$.

Except for the quantity in front of the square bracket, the rest of the right-hand side of Eq. (46) is simply a geometric factor. Namely, we have obtained an algorithm for calculating the cross section for any j. It is convenient to define a geometric factor, $\phi_j^{(x)}$, such that one can write Eq. (46) as

$$\sigma_j^{(x)}(t) = D_t(\langle v_i^{\frac{3}{5}}\rangle/\langle v_i\rangle)\phi_j^{(x)}. \quad (47)$$

The geometric factor $\phi_j^{(x)}$ is tabulated in Table I for $j = 1$ up to $j = 8$ in increments of $\frac{1}{2}$.

V. DISCUSSION OF THE RESULTS

As discussed in Appendix I, it is always possible to express the population transfer cross sections, $\sigma_j(\alpha,\gamma)$, in terms of the multipole moment relaxation cross sections, $\sigma_j^{(x)}$. [The quantity $\sigma_j(\alpha,\gamma)$ describes collisions which reorient atoms from a state $|j_\alpha\rangle$ to a state $|j_\gamma\rangle$ and vice versa.] In Fig. 1 we show the relative transfer cross sections for $j = 1$, $j = \frac{3}{2}$, and $j = 2$ states as obtained from the results in Table I and Eq. (A5). We emphasize that for a $j = 1$ state the transfer cross section for $|\Delta m| = 2$ transitions is twice that for $|\Delta m| = 1$ transitions. As pointed out in Sec. III, this ratio is a result of symmetry and is therefore independent of any collision model. For a $j = \frac{3}{2}$ state we note that the $\sigma_{3/2}(m,-m)$ are zero as discussed in the Appendix, and that the remaining cross sections are all equal. For $j = 2$ the situation is more complicated, but it is clear that the population transfer collisions are quite anisotropic. From calculations of the $\sigma_j(\alpha,\gamma)$ for higher j values, we have obtained the following results. For integer j values the largest cross section is $\sigma_j(1, -1)$, the next largest is $\sigma_j(j, j-1)$, and the smallest is $\sigma_j(j,-j+1) = \frac{1}{2}\sigma_j(j,-j)$. For half-integer j values the largest cross section is $\sigma_j(j, j-1)$, the next largest is $\sigma_j(\frac{3}{2},-\frac{1}{2})$, the smallest is $\sigma_j(j,-j+1) = \sigma_j(j,-j+2)$, and all the $\sigma_j(m,-m)$ are zero. These relationships are indicated in Fig. 2.

The multipole moment relaxation cross section can be measured by various experiments. In Hanle effect and optical double-resonance experiments,[1] the line shape of the fluorescent light

TABLE I. Computed values of $\phi_j^{(x)}$ and $\sigma_j^{(1)}/\sigma_j^{(2)}$ for j from 1 to 8 in steps of $\frac{1}{2}$. The calculations were performed using double precision arithmetic (approximately 17 decimal digits) to reduce the buildup of round-off error for the higher-j values. Above about $j = 5$ the computer time required for the calculation scales approximately as j^5. Since the $j = 8$ calculation required about $2\frac{1}{2}$ minutes of time on an IBM model 360-65 computer, we did not carry the calculation beyond this point.

x \ j	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	4	$\frac{9}{2}$
1	4.062	1.640	2.532	1.565	2.009	1.417	1.716	1.308
2	2.437	3.281	2.871	2.798	2.586	2.476	2.346	2.258
3		1.640	3.860	2.816	3.335	2.767	2.990	2.612
4			2.251	3.499	3.163	3.285	3.076	3.056
5				1.915	3.696	3.078	3.500	3.104
6					2.203	3.495	3.229	3.442
7						1.993	3.574	3.148
8							2.164	3.436
9								2.020
$\sigma_j^{(1)}/\sigma_j^{(2)}$	1.667	0.500	0.882	0.559	0.777	0.572	0.731	0.579

x \ j	5	$\frac{11}{2}$	6	$\frac{13}{2}$	7	$\frac{15}{2}$	8
1	1.521	1.228	1.388	1.160	1.284	1.101	1.204
2	2.165	2.099	2.026	1.973	1.914	1.868	1.820
3	2.737	2.462	2.546	2.331	2.393	2.220	2.267
4	2.912	2.863	2.755	2.702	2.616	2.568	2.497
5	3.285	3.003	3.095	2.884	2.933	2.767	2.796
6	3.254	3.299	3.158	3.151	3.041	3.013	2.925
7	3.545	3.236	3.417	3.184	3.278	3.096	3.147
8	3.230	3.487	3.325	3.411	3.279	3.303	3.197
9	3.472	3.161	3.543	3.298	3.479	3.284	3.382
10	2.131	3.368	3.209	3.490	3.352	3.463	3.346
11		2.027	3.384	3.151	3.523	3.326	3.506
12			2.103	3.303	3.180	3.475	3.359
13				2.022	3.309	3.129	3.494
14					2.076	3.243	3.147
15						2.011	3.242
16							2.051
$\sigma_j^{(1)}/\sigma_j^{(2)}$	0.703	0.585	0.685	0.588	0.671	0.589	0.661

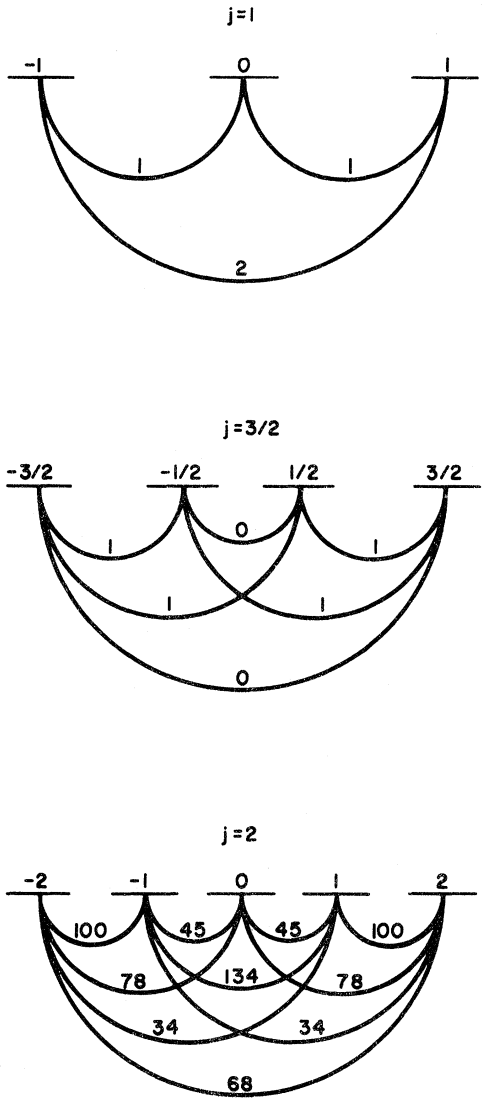

FIG. 1. Relative population transfer rates for $j=1$, $j=\frac{3}{2}$, and $j=2$ states. The horizontal lines represent the magnetic sublevels, labeled by their m values, and the numbers on the lines joining them are the relative cross sections for collision-induced transfers between the indicated sublevels. Different scale factors have been used for the different j values. Use the results in Table I and in Eqs. (47) and (A.5) to obtain absolute cross sections.

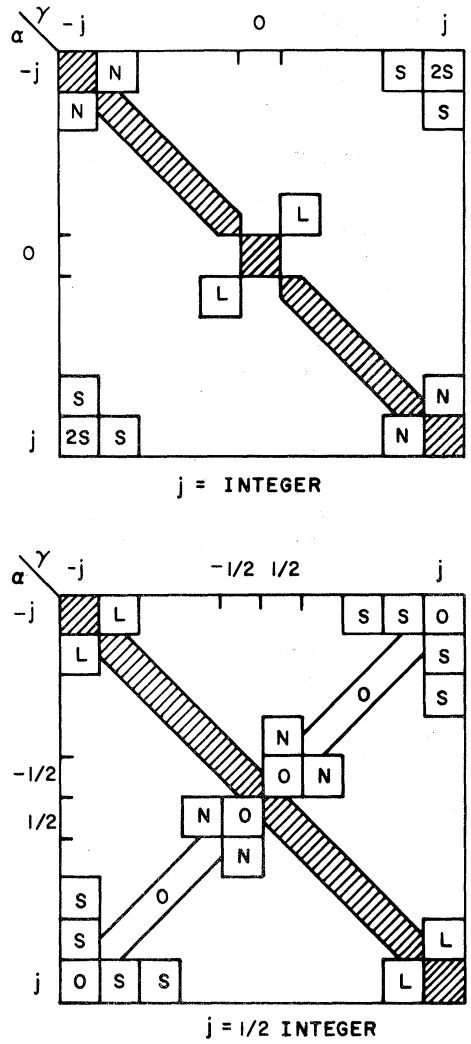

FIG. 2. Schematic population transfer cross-section matrices, $\sigma_j(\alpha,\gamma)$. The L indicates the largest cross section, the N the next to largest, and the S the smallest. The $2S$ indicates a cross section twice the smallest. The main diagonals are shaded to indicate that these do not represent population transfers. Note that for half-integer j values all the elements on the cross diagonal are zero.

emitted from an ensemble of excited atoms in a sufficiently weak magnetic field provides information on the cross sections $\sigma_j^{(1)}$ and $\sigma_j^{(2)}$, more commonly referred to as the "orientation" cross section and the "alignment" cross section, respectively. In the following paper we describe a new method of measuring $\sigma_j^{(1)}$ and $\sigma_j^{(2)}$ for states involved in laser oscillations.[5] In Fig. 3 we plot $\phi_j^{(1)}$, $\phi_j^{(2)}$ and the ratio $\sigma_j^{(1)}/\sigma_j^{(2)}$ as functions of j. For integer j the ratio decreases drastically from $\frac{5}{3}$ for $j=1$ to 0.88 for $j=2$ and then slowly approaches its asymptotic value. For half-integer j the ratio is $\frac{1}{2}$ for $j=\frac{3}{2}$, and reaches its asymptotic value somewhat earlier. The ratio $\frac{1}{2}$ for $j=\frac{3}{2}$ is in good agreement with the experimental results of Gallagher[13] for Rb atoms in the $5p^2P_{3/2}$ state colliding with Ne or Ar atoms.

The higher multipole relaxation cross sections have not yet been measured. As one sees from Table I, these are comparable with or larger than $\sigma^{(1)}$ and $\sigma^{(2)}$, and are important to provide a complete understanding of the collision-induced

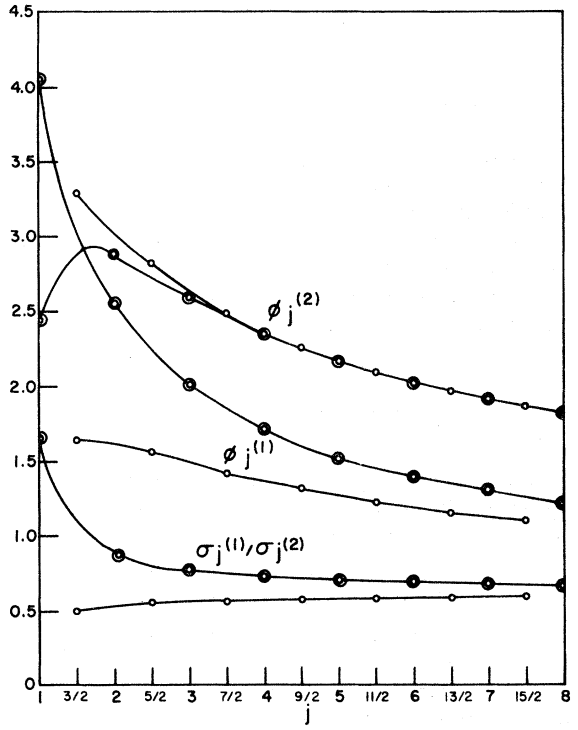

FIG. 3. Plots of $\phi_j^{(1)}$, $\phi_j^{(2)}$ and $\sigma_j^{(1)}/\sigma_j^{(2)}$ as functions of j. The integer and half-integer cases are indicated by double and single circles, respectively. The curves drawn through the calculated points are simply to indicate trends, and have no particular physical significance. The upper two curves are for $\phi_j^{(2)}$, the middle two for $\phi_j^{(1)}$, and the lower two for $\sigma_j^{(1)}/\sigma_j^{(2)}$.

relaxation. The higher multipole moments contribute only through the nonlinear response of the medium, but it may be possible to measure such quantities by studying the saturation effect of a Hanle-effect experiment by a high-power laser. Photon-echo experiments may also provide measurements of the higher-moment relaxation rates although it might be difficult to separate the various quantities.

ACKNOWLEDGMENTS

We wish to express our appreciation to Dr. J. P. Gordon for helpful discussions.

APPENDIX I

Relation Between the Multipole Moment Relaxation Rate Constant $\gamma_j^{(x)}$ and the Collision Matrix $\Gamma(j|\alpha\beta;\gamma\delta)$

As mentioned in the text, the equation expressing the decay of the density matrix for a state of a given j in the "lm" representation is given by

$$\dot{\rho}_{j_\alpha j_\beta}(t) = -\sum_{\gamma\delta}\langle\Gamma(j|\alpha\beta;\gamma\delta)\rangle\,\rho_{j_\gamma j_\delta}(t). \quad \text{(A1)}$$

Here the angular bracket is defined by the equivalence of Eq. (A1) and Eq. (4) of the text.

In the spherical tensor representation, the equation for the decay of $\rho_q^{(x)}$ is given by

$$\dot{\rho}_q^{(x)} = -\gamma_j^{(x)}\rho_q^{(x)}. \quad \text{(A2)}$$

Carrying out the transformation given in Eq. (9), and making use of the orthogonality property of the 3-j symbol, we obtain

$$\langle\Gamma(j|\alpha\beta;\gamma\delta)\rangle = \sum_{xq}(-1)^{\gamma-\alpha}\gamma_j^{(x)} \times(2x+1)\begin{pmatrix} j & x & j \\ -\gamma & -q & \delta\end{pmatrix}\begin{pmatrix} j & x & j \\ -\alpha & -q & \beta\end{pmatrix}. \quad \text{(A3)}$$

Since the excitation transfer and the reorientation of the angular momentum of the atom contribute independently to the relaxation of the multipole moment, we separate out from Eq. (A3) the part which describes only the reorientation process, and obtain

$$\langle\Gamma(j|\alpha\beta;\gamma\delta)\rangle_{\mathrm{RE}} = \sum_{xq}(-1)^{\gamma-\alpha}[\gamma_j^{(x)} - \gamma_j^{(0)}] \times(2x+1)\begin{pmatrix} j & x & j \\ -\gamma & -q & \delta\end{pmatrix}\begin{pmatrix} j & x & j \\ -\alpha & -q & \beta\end{pmatrix}$$

$$\text{with} \quad \alpha\neq\gamma \quad \text{and} \quad \beta\neq\delta, \quad \text{(A4)}$$

where the subscript RE indicates reorientation.

It is useful to define a quantity, $\sigma_j(\alpha,\gamma)$, called the population transfer cross section, as

$$\sigma_j(\alpha,\gamma) \equiv -\langle\Gamma(j|\alpha\alpha;\gamma\gamma)\rangle_{\mathrm{RE}}/n\langle v_i\rangle = -\sum_x(-1)^{\gamma-\alpha}\Lambda_j^{(x)} \times(2x+1)\begin{pmatrix} j & x & j \\ -\alpha & 0 & \alpha\end{pmatrix}\begin{pmatrix} j & x & j \\ -\gamma & 0 & \gamma\end{pmatrix}. \quad \text{(A5)}$$

The quantity $\sigma_j(\alpha,\gamma)$ has the properties

$$\sigma_j(\alpha,\gamma) = \sigma_j(-\alpha,-\gamma) = \sigma_j(\gamma,\alpha). \quad \text{(A6)}$$

The population transfer cross section $\sigma_j(\alpha,\gamma)$ describes collisions which transfer atoms from one orientation to another. For a $j=1$ state, one always has $\Lambda^{(1)}=\frac{5}{3}\Lambda^{(2)}$; it is then simple to show by Eq. (A5) that

$$\sigma_1(1,-1)/\sigma_1(1,0) = 2. \quad \text{(A7)}$$

By setting $\gamma=-\alpha$ in Eq. (A5) we obtain the cross section for transfers from the state $|j_\alpha\rangle$ to the state $|j_{-\alpha}\rangle$ as

$$\sigma_j(\alpha,-\alpha) = -\sum_x(-1)^x\Lambda_j^{(x)}(2x+1)\begin{pmatrix} j & j & x \\ \alpha & -\alpha & 0\end{pmatrix}^2, \quad \text{(A8)}$$

or by using Eq. (12)

$$\sigma_j(\alpha,-\alpha)=-\sum_J G(J)\begin{pmatrix} j & j & J\\ -\alpha & \alpha & 0\end{pmatrix}\begin{pmatrix} j & j & J\\ \alpha & -\alpha & 0\end{pmatrix}. \quad \text{(A9)}$$

For half-integer j values we can sum over α in Eq. (A8) to obtain the simple result

$$\sum_\alpha \sigma_j(\alpha,-\alpha)=-\sum_x (-1)^x \Lambda_j^{(x)} \quad (j=\tfrac{1}{2}\text{-integer}). \quad \text{(A10)}$$

It has recently been shown that for weak collisions the $\sigma_j(\alpha,-\alpha)$ are all zero for half-integer j values[13,14]; thus for such collisions Eq. (A10) becomes simply

$$\sum_x (-1)^x \Lambda_j^{(x)}=0 \quad (j=\tfrac{1}{2}\text{-integer}). \quad \text{(A11)}$$

The numerical results given in Table I all satisfy Eq. (A11) (for half-integer j values). It is clear that for the interaction potential we have used, the $\sigma_j(j,-j)$ must be zero since such a transition requires an electron spin flip but the potential does not involve the spin coordinate. It is less clear why the other $\sigma_j(\alpha,-\alpha)$ are also zero.

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