dropped in (6). The choice of γ which eliminates the first-order contribution will also eliminate the first contribution. The second-order potentials will enter identically in the 3-3 and 4-4 equations by virtue of condition (16) and so the process of forming (15) from (14) will cancel this contribution. Therefore the expansion in (15) will be accurate up to third-order terms.

---

*Research supported by the Office of Naval Research under Contract No. N00014-72-A-0406-0004 and by CUNY Faculty Research Award No. 1657.

[1] J. C. Y. Chen and K. M. Watson, Phys. Rev. **174**, 152 (1968).

[2] H. G. Bennewitz, H. Busoc, H. D. Dohmann, D. E. Oates, and W. Schrader, Phys. Rev. Lett. **29**, 533 (1972).

[3] The effect has been measured in Ref. 2 and predicted theoretically. See M. H. Mittleman, Phys. Rev. 188, 221 (1969).

PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Coherence Transfer in Magnetic Fields*

W. E. Baylis
Physics Department, University of Windsor, Windsor, Ontario, Canada

(Received 10 July 1972)

Some results recently discussed by Chiu for interatomic coherence transfer are shown to have a simple physical interpretation, to be independent of collision model assumed, and to be applicable also to *intra*-atomic coherence transfer. A derivation using density matrices is presented which takes both depolarizing collisions and backtransfer of coherence into account.

I. INTRODUCTION

In a recent article Chiu[1] has detailed a calculation of nonresonant coherence transfer between atoms in a magnetic field. The calculation is intended to explain the type of experiment performed by Gough[2] in which a mixture of Hg and Cd atoms is irradiated with polarized resonance radiation of Hg, and the resulting sensitized fluorescence of Cd is then observed by means of a "sensitized Hanle experiment" to be partially polarized. In Chiu's calculation a pure dipole-dipole interaction is assumed and applied in a perturbation treatment to first order both in the electronic transition and in the internuclear motion; depolarizing collisions and backtransfer of coherence are neglected [starting in his fundamental equation (1.29)].

It is pointed out here that (i) a very simple interpretation exists for many of Chiu's results, (ii) these results are independent of the collision model, and (iii) they are even applicable to coherence transfer between states of the same atom (*intra-atomic* coherence transfer). A general derivation is presented which also includes collisional depolarization and coherence backtransfer.

Gough's experiments were first explained by Cheron and Barrat,[3] who based their density-matrix calculation on a collisional "selection rule" proposed by Franzen.[4] Intra-atomic coherence transfer was considered by Elbel, Niewitecka, and Krause,[5] who reported transfer of orientation from the $^2P_{1/2}$ to the $^2P_{3/2}$ state of alkali-metal atoms in collision with various foreign gases. They observed a Hanle signal in the sensitized fluorescence and proposed a simple model to explain their results.

II. SIMPLE PHYSICAL PICTURE

In an early paper, Hanle[6] gave a simple classical explanation of what has since become known as the Hanle effect[7]: Linearly polarized light excites an electric dipole to oscillate in the direction of polarization, and a constant magnetic field (say in the z direction) by means of the Lorentz force causes the dipole to rotate in the xy plane at the Larmor frequency ω. Since the radiation pattern for an oscillating dipole varies as $\sin^2\varphi$ in a direction φ from the diploe axis, and since the total intensity radiated by the dipole at time t is proportional to $e^{-\Gamma t}$, the intensity observed in the xy plane at an angle φ from the direction of initial polarization radiated by an ensemble of continuously excited oscillators is proportional to

$$2\Gamma\int_0^\infty dt\, e^{-\Gamma t}\sin^2(\varphi+wt)=1+\frac{\beta\sin 2\varphi-\cos 2\varphi}{1+\beta^2}, \tag{1}$$

where $\beta=2\omega/\Gamma$. Consequently, the intensity observed as a function of magnetic field when φ is a multiple of $\frac{1}{2}\pi$ is a Lorentz curve, the half-width of which can be used to determine the mean lifetime of the oscillators, $1/\Gamma$. Although directly applicable only in atomic transitions between a $J=0$ ground state and a $J=1$ excited state, the simple physical picture provided by Hanle's original model has made this model very popular.

When observed in sensitized fluorescence, the Hanle effect involves two excited states, say $|1\rangle$ and $|2\rangle$, each with a set of nearly degenerate sublevels and with possibly distinct lifetimes (Γ_1^{-1} and Γ_2^{-1}) and precession frequencies (ω_1 and ω_2). The states may be associated either with the same atom or with different atoms. Let the optical excitation be to state $|1\rangle$, whereas radiation is to be observed from $|2\rangle$. Excitation transfer occurs at time $t_2=0$, a time t_1 after the initial excitation, and it is assumed that the coherence is not all lost during the transfer. The dipole of state $|1\rangle$ will have rotated an angle $\omega_1 t_1$ by the time of excitation transfer, and by the time emitted radiation is observed (t_2), dipole $|2\rangle$ will have rotated an additional angle $\omega_2 t_2$. The field-dependent part of the sensitized radiation is thus proportional to

$$2\Gamma_1\Gamma_2\int_0^\infty dt_1 e^{-\Gamma_1 t_1}\int_0^\infty dt_2 e^{-\Gamma_2 t_2}\sin^2(\omega_1 t_1+\omega_2 t_2+\varphi)$$
$$=1+[(\beta_1\beta_2-1)\cos 2\varphi+(\beta_1+\beta_2)\sin 2\varphi]\times[(1+\beta_1^2)(1+\beta_2^2)]^{-1}, \quad (2)$$

where $\beta_i=2\omega_i/\Gamma_i$. From the special cases $\varphi=0$ and $\frac{1}{2}\pi$, Chiu's results (2.10) and (3.12) for the magnetic field dependence of the sensitized fluorescence are regained. The backtransfer of coherence has not yet been considered, but depolarizing collisions are properly taken into account by interpreting Γ_i^{-1} as the lifetime of coherence in state $|i\rangle$. Equation (2) has been derived for excitation by linearly polarized light and hence for the "alignment" type of coherence. If, instead, circularly polarized light is used to excite orientation (a magnetic dipole instead of an oscillating electric dipole) in states $|1\rangle$ and $|2\rangle$, the appropriate equation is obtained from Eq. (2) by replacing φ and ω by $\frac{1}{2}\varphi$ and $\frac{1}{2}\omega$, respectively.

III. GENERAL FORMULATION OF COHERENCE TRANSFER

A more general derivation including backtransfer of coherence is easily derived in terms of density matrices.[3,8] It is assumed that states $|1\rangle$ and $|2\rangle$ with total angular momenta J_1 and J_2 are sufficiently isolated that off-diagonal elements of the density matrix connecting them are negligible, and further that transitions to other excited states can be neglected. The system can then be described by two density matrices, $\rho^{(1)}$ and $\rho^{(2)}$, one for each excited state. In the interaction representation the equations of motion are[8]

$$\frac{d}{dt}\rho^{(1)}=-\Gamma_1\rho^{(1)}-i\omega_1[J_{1z},\rho^{(1)}]+\Gamma_{12}\rho^{(2)}+S,$$
$$\frac{d}{dt}\rho^{(2)}=-\Gamma_2\rho^{(2)}-i\omega_2[J_{2z},\rho^{(2)}]+\Gamma_{21}\rho^{(1)}, \quad (3)$$

where the Liouville-space operator Γ_{ij} gives the rate of collision-induced excitation transfer from $|j\rangle$ to $|i\rangle$, and S represents the light source. We expand Eq. (3) in irreducible tensor operators[9]:

$$\rho=\sum_{lm}\rho_{lm}T^{lm};\quad \rho_{lm}\equiv\mathrm{Tr}(\rho T_m^{l}),$$

and similarly for S, and use the isotropy of the collisions to find[10]

$$\frac{d}{dt}\rho_{lm}^{(1)}=-\Gamma_{1,l}\rho_{lm}^{(1)}-im\omega_1\rho_{lm}^{(1)}+\Gamma_{12,l}\rho_{lm}^{(2)}+S_{lm},$$
$$\frac{d}{dt}\rho_{lm}^{(2)}=-\Gamma_{2,l}\rho_{lm}^{(2)}-im\omega_2\rho_{lm}^{(2)}+\Gamma_{21,l}\rho_{lm}^{(1)}. \quad (4)$$

The steady-state solution of Eq. (4) is readily found to be

$$\rho_{lm}^{(2)}=\frac{\Gamma_{12,l}S_{lm}}{(\Gamma_{1,l}+im\omega_1)(\Gamma_{2,l}+im\omega_2)-\Gamma_{12,l}\Gamma_{21,l}}. \quad (5)$$

If, through the detection of polarized radiation, our monitoring efficiency of the l, $\pm m$ components of ρ is $M^{(l,m)}$,[11] then the detected intensity is

$$I=\sum_{lm}M^{(l,m)}\rho_{lm}^{(2)}$$
$$=\sum_{lm}M^{(l,m)}S_{lm}\times\frac{\Gamma_{12,l}(\Gamma_{1,l}\Gamma_{2,l}-\Gamma_{12,l}\Gamma_{21,l}-m^2\omega_1\omega_2)}{|(\Gamma_{1,l}+im\omega_1)(\Gamma_{2,l}+im\omega_2)-\Gamma_{12,l}\Gamma_{21,l}|^2}. \quad (6)$$

In the above formulation $\Gamma_{i,l}$ is the total decay rate, including collisional depolarization, for the lth multipole of state $|i\rangle$ and $\Gamma_{ij,l}$ is the rate at which l-multipole coherence is transferred to state $|i\rangle$ from state $|j\rangle$. Note that by their definition $\Gamma_{j,l}\geq\Gamma_{ij,l}$.

We emphasize the generality of Eq. (6): It is applicable to all collision models. Equation (6) includes effects of both collisional depolarization and, through the presence of Γ_{21}, the backtransfer of coherence, and it is applicable to both *interatomic* and *intra-atomic* coherence transfer. The details of the collisions will be contained in the expressions for the transfer rates $\Gamma_{ij,l}$ and for the relaxation rates $\Gamma_{i,l}$. These expressions include the dependence on interatomic potentials and on densities, and of course such dependence is different for interatomic and intra-atomic coherence transfer.

If the nuclear spin is nonzero, transitions may be important among several hyperfine multiplets, and, furthermore, in the presence of an external field a partial decoupling of nuclear and electronic angular momenta may occur. The above formulation is then inadequate and should be extended to include several excited states and the hyperfine interaction.

*Research supported by the National Research Council of Canada.

[1] L.-Y. C. Chiu, Phys. Rev. A **5**, 2053 (1972).

[2] W. Gough, Proc. Phys. Soc. Lond. **90**, 287 (1967).

[3] B. Cheron and J. P. Barrat, C.R. Acad. Sci. B **266**, 1324 (1968).

[4] W. Franzen, Phys. Rev. **115**, 850 (1959). This selection rule was also used by Gough (Ref. 2) to estimate the degree of coherence transfered during collision.

[5] M. Elbel, B. Niewitecka, and L. Krause, Can. J. Phys. **48**, 2996 (1970).

[6] W. Hanle, Z. Phys. **41**, 164 (1927).

[7] See, for example, R. deZafra and W. Kirk, Am. J. Phys. **35**, 573 (1967), and references therein.

[8] U. Fano, Rev. Mod. Phys. **29**, 74 (1957); J. P. Barrat and C. Cohen-Tannoudji, J. Phys. Radium **22**, 329 (1961); J. Phys. Radium **22**, 443 (1961); W. Happer, Rev. Mod. Phys. **44**, 169 (1972).

[9] A. Omont, J. Phys. Radium 26, 26 (1965); M. I. D'Yakonov and V. I. Perel, Zh. Eksp. Teor. Fiz. 47, 1483 (1964) [Sov. Phys.-JETP 20, 997 (1965)]; M. I. D'Yakonov, Zh. Eksp. Teor. Fiz. 47, 2213 (1964)[Sov. Phys.-JETP 20, 1484 (1965)].

[10] Coupled equations for the special case of orientation ($l=1$) transfer between different isotopes of the same element have been given by B. Dodsworth and A. Omont, Phys. Rev. Lett. **24**, 198 (1970).

[11] See, for example, C. G. Carrington, J. Phys. B 4, 1222 (1971), especially Eq. (14).

PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Natural Analysis of the ^2S and ^2P States of the Lithiumlike Ions*

Vedene H. Smith, Jr.†
Lehrstuhl für Theoretische Chemie der Technischen Universität München, West Germany

Richard Edwin Brown and Ajit J. Thakkar
Chemistry Department, Queen's University, Kingston, Ontario, Canada

(Received 13 September 1972)

Since two recent investigations revealed different structures for the one-electron reduced-density matrix (one matrix) of the Weiss wave function of the lowest (^2P) state of lithium, we have reanalyzed the Weiss wave functions for both the lowest ^2S and ^2P states of the three-electron ions. Although Weiss employed "^2S restrictions" in the construction of his ^2P wave functions, their natural spin orbitals are not as spatially symmetry adapted as they are for the ^2S states.

The natural analysis[1] of correlated wave functions has proved in recent years[2] to be a powerful tool for understanding of the correlation problem and the comparison of wave functions of apparently dissimilar form. This method involves the determination of the eigenfunctions χ_j [natural spin orbitals (NSO)] and eigenvalues ν_j (occupation numbers) of the one-electron reduced-density matrix (one matrix) $\gamma_\Psi(x_1, x_1')$. Here $\gamma_\Psi(x_1, x_1')$ is defined by

$$\gamma_\Psi(x_1, x_1') = N \int \Psi(x_1, x_2, \ldots, x_n) \times \Psi^*(x_1', x_2, \ldots, x_n)\, dx_2 \cdots dx_n \,, \tag{1}$$

where N is the number of electrons and x_i denotes the space and spin coordinates of electron i. In terms of the $\chi_j(x)$ and ν_j,

$$\gamma_\Psi(x_1, x_1') = \sum_{j=1} \nu_j \chi_j(x_1) \chi_j^*(x_1') \tag{2a}$$

and

$$\int \gamma_\Psi(x_1, x_1') \chi_j(x_1')\, dx_1' = \nu_j \chi_j(x_1) \,, \tag{2b}$$

where

$$\sum_{j=1} \nu_j = N \tag{2c}$$

and the ν_j's are ordered such that

$$0 \le \nu_{j+1} \le \nu_j \le 1 \,. \tag{2d}$$

Natural analyses have been performed for a number of atomic systems of ^1S symmetry; in particular for two-,[3] four-,[4] six-,[5] and ten-electron[6] atomic ions. For atomic wave functions of ^1S symmetry, the NSO are eigenfunctions of the one-electron operators l^2, l_z, s^2, s_z, and i (the inversion operator). As a result, the eigenvalue spectrum possesses degeneracies of order $2(2l+1)$ between all NSO with the same quantum number l.[7]

In the construction of correlated wave functions for atomic states which are not of ^1S symmetry, one is faced with the additional problem of describing properly the orbital ($L \ne 0$) and spin ($S \ne 0$) polarization effects in addition to the normal correlation problem found in the more symmetric ^1S states. This polarization leads to a quite different structure of the one matrix. In particular, Larsson and Smith[8] have analyzed a number of wave functions for the Li (^2S) ground state and demonstrated the effects of spin polarization, the only type present for ^2S states. Here the NSO eigenvalue spectrum possesses degeneracies of order