AN ABSTRACT OF THE THESIS OF

RAJENDRA PRASAD SRIVASTAVA for the DOCTOR OF PHILOSOPHY
(Name of student) (Degree)

in Physics presented on May 3, 1972
(Major) (Date)

TITLE: EFFECTS OF COUPLED ATOMIC STATES ON THE RESONANCE SCATTERING OF RADIATION

Abstract approved: Redacted for Privacy
Dr. Peter R. Fontana

The excitation and decay probabilities for resonance scattering of radiation from an atom with two coupled excited states and one ground state in an external static field are calculated as a function of time and frequency. Various oscillatory behaviors are found in all the probabilities. These oscillations depend on the frequency of radiation, the external coupling and the energy difference between the excited states. For the case where one of the excited states is non-decaying, a "hole" is observed in the emission line at the frequency equal to the frequency difference between the ground state and the unperturbed non-decaying excited state. For non-degenerate excited states, the two lines in the emitted beam have unequal linewidths which depend on the energy difference between the excited states and the external coupling. For degenerate excited states, the two lines have equal linewidth which is half of the linewidth of the decaying state. For two decaying excited states, one of the two

lines in the scattered beam is suppressed and the other is enhanced by the external coupling. For this case crossing and anticrossing signals are calculated in the total intensity of the scattered beam. These signals are computed for the 2^2P state in Li^7 as a function of an external magnetic field.

Effects of Coupled Atomic States on the
Resonance Scattering of Radiation

by

Rajendra Prasad Srivastava

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

June 1972

APPROVED:

Redacted for Privacy

Associate Professor of Physics
in charge of major

Redacted for Privacy

Chairman of Department of Physics

Redacted for Privacy

Dean of the Graduate School

Date thesis is presented May 3, 1972

Typed by Madhuri for Rajendra Prasad Srivastava

ACKNOWLEDGEMENT

I am deeply indebted to Professor Peter R. Fontana for his guidance and invaluable suggestions throughout the course of this study. I would like to express my thanks to Dr. Charles W. Drake for helpful conversations and suggestions.

The computor programming and graphic display of my work would have been impossible without the help from Dr. Timothy G. Kelley and Dr. David V. Grillot. I would like to express my gratefulness to them.

Finally, my wife, Madhuri, deserves special thanks for her moral support and her assistance in typing.

TABLE OF CONTENTS

LIST OF FIGURES

EFFECTS OF COUPLED ATOMIC STATES ON THE RESONANCE SCATTERING OF RADIATION

I. INTRODUCTION

The study of scattering processes has always been of significant importance in Physics. The photon scattering, in particular, has provided information about energies, life-times and fine and hyperfine interactions of atoms, molecules and solids. The scattering of radiation has also been studied in the presence of an external perturbation.

Colegrove and others (1) demonstrated in 1959 that, under certain conditions, the crossing of two Zeeman levels of two excited states of an atom in a magnetic field produces an interference term in the scattered beam. This interference term has spatial dependence and also a dependence on the energy difference between the two levels. The study of such signals provides experimental values for the fine and the hyperfine structure constants of the levels involved. In 1963, Eck and others (2) found another kind of signal called anticrossing signal. This signal arises due to the presence of a perturbation which couples the two Zeeman levels which cross in the absence of the perturbation. Himmell and Fontana (3) have investigated such signals in atomic Hydrogen.

Hearn and Fontana (4) used the quantum theory of radiation developed by Heitler and Ma (5) to investigate the resonance scattering of radiation from a two-atom system. They have studied the frequency distribution of the scattered radiation as a function of the interatomic distance. The present work investigates the resonance scattering of radiation from a single atom with two excited states and one ground state. The two excited states are coupled by an external static perturbation. The incident radiation is assumed to be of constant intensity I_o per unit area per unit solid angle per unit frequency (white light). The method of solving the wave equation is the same as used by Hearn and Fontana (4). This approach gives all the probabilities including the final state probability as a function of time whereas the Wigner Weisskopf (6) approach does not give the probability for the final state directly.

The absorption and the emission of radiation is studied here as a function of time and frequency for different special cases. These special cases are: (i) one of the excited states is non-decaying. (ii) both the excited states decay with equal decay constants. The effects of the external coupling on the lineshape and linewidth of the scattered radiation is investigated.

The intensity of the scattered radiation is calculated for a given direction and polarization of the incident and the scattered beams. As an application, this intensity is computed for the 2^2P state in Li^7 and is compared with the experimental signals observed by Wieder and Eck (7).

II. GENERAL THEORY

The system, under study, consists of an isolated atom which interacts with a radiation field and a time independent external perturbation. The atom is assumed to have two excited states and one ground state. The external perturbation couples only the two excited states. Initially, the atom is in the ground state and a beam of white light (a continuous spectrum of radiation with constant energy I_o per unit area per unit solid angle and per unit frequency) is incident on it.

A. Method of Solution of the Wave Equation

The method used for solving the wave equation is a transformation of the wave equation into energy space (8). The interaction representation is used. The units are such that $\hbar = c = m = 1$ where $\hbar$ is the Plank constant divided by 2π, c the speed of light in vacuum and m the mass of the electron at rest.

If $|\Psi(t)\rangle$ is the wave vector in the Schrödinger representation, then

$$|\Psi'(t)\rangle = e^{iH_o t}\,|\Psi(t)\rangle \qquad (2\text{-}1)$$

is the wave vector in the interaction representation. H_o is the Hamiltonian of the atom plus that of the radiation field, when the two are non-interacting and there is no external perturbation field. The Hamiltonian of the whole system in the Schrödinger representation then is

$$\mathcal{H} = H_o + H' \tag{2-2}$$

where H' consists of V, the external perturbation, plus H, the interaction of the atom with radiation field.

In the interaction representation, the wave equation is given by the expression

$$i \frac{\partial}{\partial t} |\Psi'(t)\rangle = e^{iH_o t} H' e^{-iH_o t} |\Psi'(t)\rangle \; . \tag{2-3}$$

Considering only processes involving one photon, the state vector of the system in the interaction representation is given by

$$|\Psi'(t)\rangle = b_o(t)|o\rangle + \sum_i b_i(t)\,|i\rangle$$

$$+ \sum_j b_j(t)\,|j\rangle + \sum_f b_f(t)\,|f\rangle \tag{2-4}$$

where $|o\rangle$ represents the ground state; $|i\rangle$, $|j\rangle$ the excited states with a photon absorbed and $|f\rangle$ the final states. All these states are the eigenstates of H_o. In terms of the atomic and photon's states, they are written as

$$|o\rangle = |c\rangle|o\rangle_R$$

$$|i\rangle = |a\rangle|-k_\sigma\rangle_R$$

$$|j\rangle = |b\rangle|-k_\sigma\rangle_R$$

and

$$|f\rangle = |c\rangle|-k_\sigma\rangle_R |k_\lambda\rangle_R \; .$$

The state vectors $|0\rangle_R$, $|-k_r\rangle_R$ and $|k_\lambda\rangle_R$ represent the states of the radiation field with no photons present, an absorbed photon with wave vector $\vec{k}_r$ and polarization $\hat{e}_r$ and an emitted photon with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$, respectively.

In Eq.(2-4) the summations over i and j are over frequency, direction and polarization of the incident radiation, and the summation over f is over frequencies, directions and polarizations of the incident and the emitted radiations.

The state vector $|\Psi'(t)\rangle$ can be written in a simplified form as

$$|\Psi'(t)\rangle = \sum_m b_m(t)\,|m\rangle \tag{2-5}$$

where m includes all the quantum numbers defining the eigen states of H_0 in the interaction representation.

By inserting Eq.(2-5) into Eq.(2-3), multiplying by $\langle n|$ and integrating over all space, one obtains the follwing set of equations

$$i\,\frac{d}{dt}\,b_n(t) = \sum_m H'_{nm}\,b_m(t)\,e^{i(E_n-E_m)t} \tag{2-6}$$

where H'_{nm} denotes the matrix elements of H':

$$H'_{nm} = \langle n|\,H'\,|m\rangle \ . \tag{2-7}$$

Since at t = 0, the system is in the ground state $|0\rangle$, the initial conditions are:

$$\begin{aligned} b_0(0) &= 1 \ , \\ b_n(0) &= 0 \quad \text{for} \quad n \neq 0 \end{aligned} \tag{2-8}$$

and

$$b_n(t) = b_o(t) = 0 \quad \text{for} \quad t < 0 \ .$$

In order to satisfy these conditions a term involving a Dirac delta function is added (8) in Eq.(2-6), which gives

$$i \frac{d}{dt} b_n(t) = \sum_m H'_{nm} \, b_m(t) \, e^{i(E_n - E_m)t} + i \delta_{no} \, \delta(t). \qquad (2\text{-}9)$$

To solve Eq.(2-9) the $b_n(t)$ are transformed by using the following Fourier transformation:

$$b_n(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \;\; G_n(E) \, e^{i(E_n - E)t} \ . \qquad (2\text{-}10)$$

In a similar fashion the representation of the Dirac delta function is used:

$$i \, \delta(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \;\; e^{i(E_o - E)t} \ . \qquad (2\text{-}11)$$

With these transformations, Eq.(2-9) reduces to

$$\int_{-\infty}^{\infty} dE \, (E - E_n) \, G_n(E) \, e^{i(E_n - E)t}$$

$$= \int_{-\infty}^{\infty} dE \, \left[\sum_m H'_{nm} \, G_m(E) + \delta_{no} \right] e^{i(E_n - E)t} \ . \qquad (2\text{-}12)$$

This equation is satisfied if

$$(E-E_n)G_n(E) = \sum_m H'_{nm} G_m(E) + \delta_{no} \quad . \tag{2-13}$$

This gives a set of equations for the $G(E)$:

$$(E-E_o)G_o(E) = H'_{oo}G_o(E) + \sum_i H'_{oi}G_i(E) + \sum_j H'_{oj}G_j(E)$$

$$+ \sum_f H'_{of} G_f(E) + 1 \quad , \tag{2-14}$$

$$(E-E_i)G_i(E) = H'_{io}G_o(E) + \sum_{i'} H'_{ii'} G_{i'}(E)$$

$$+ \sum_j H'_{ij} G_j(E) + \sum_f H'_{if} G_f(E) \quad , \tag{2-15}$$

$$(E-E_j)G_j(E) = H'_{jo} G_o(E) + \sum_i H'_{ji} G_i(E)$$

$$+ \sum_{j'} H'_{jj'} G_{j'}(E) + \sum_f H'_{jf} G_f \quad , \tag{2-16}$$

and

$$(E-E_f)G_f(E) = H'_{fo} G_o(E) + \sum_i H'_{fi} G_i \tag{2-17}$$

$$+ \sum_j H'_{fj} G_j(E) + \sum_{f'} H'_{ff'} G_{f'}(E)$$

where

$$\begin{aligned} E_o &= E_c \\ E_i &= E_a - k_\sigma \\ E_j &= E_b - k_\sigma \\ E_{\bar{j}} &= E_c - k_\sigma + k_\lambda \quad . \end{aligned} \tag{2-18}$$

Since only processes involving single photon are considered, the following matrix elements of H' are zero;

$$\begin{aligned} H'_{fo} &= 0 \\ H'_{of} &= 0 \end{aligned} \tag{2-19}$$

and also one finds that

$$\begin{aligned} H'_{ii'} &= V_{aa}\,\delta_{k_\sigma k'_\sigma} \\ H'_{jj'} &= V_{bb}\,\delta_{k_\sigma k'_\sigma} \\ H'_{ij'} &= V_{ab}\,\delta_{k_\sigma k'_\sigma} \\ H_{ff'} &= V_{cc}\,\delta_{k_\sigma k'_\sigma} \\ H'_{oi} &= \langle o|H+V|i\rangle = \langle o|H|i\rangle \\ H'_{oj} &= \langle o|H+V|j\rangle = \langle o|H|j\rangle \\ H'_{if'} &= H_{if}\,\delta_{k_\sigma k'_\sigma} \\ H'_{jf'} &= H_{jf}\,\delta_{k_\sigma k'_\sigma} \end{aligned} \tag{2-20}$$

where

$$V_{lm} = \langle l|V|m\rangle \quad ; \quad l, m = a, b, c. \tag{2-21}$$

Substituting these matrix elements into Eq.(2-14) to Eq.(2-17), one gets the following equations

$$(E-E'_o)\,G_o(E) = \sum_i H_{oi}\,G_i(E) + \sum_j H_{oj}\,G_j(E) + 1 \tag{2-22}$$

$$(E-E_i')G_i(E) = H_{io}G_o(E) + V_{ab}G_j(E) + \sum_f H_{if}G_f(E) \quad (2\text{-}23)$$

$$(E-E_j')G_j(E) = H_{jo}G_o(E) + V_{ba}G_i(E) + \sum_f H_{jf}G_f(E) \quad (2\text{-}24)$$

and

$$(E-E_f')G_f(E) = H_{fi}G_i(E) + H_{fj}G_j(E) \quad (2\text{-}25)$$

where

$$\begin{aligned} E_o' &= E_c + V_{cc} \\ E_i' &= E_i + V_{aa} \\ E_j' &= E_j + V_{bb} \\ E_f' &= E_f + V_{cc} \ . \end{aligned} \quad (2\text{-}26)$$

The summation over f in Eq.(2-23) and Eq.(2-24) is over frequency, direction and polarization of the emitted radiation only, because the matrix elements H_{if} and H_{jf} are zero if the state $|f\rangle$ contains an absorbed photon which differs from the photon in $|i\rangle$ and $|j\rangle$, respectively.

Equation(2-25) does not have a unique solution for $G_f(E)$ because division by $(E - E_f')$ is not unique. A solution of the equation, which satisfies the initial condition, however, can be obtained in the following way (8)

$$G_f(E) = \zeta(E-E_f')\left[H_{fi}G_i(E) + H_{fj}G_j(E)\right] \quad (2\text{-}27)$$

where $\zeta(E-E_f)$ is the Zeta function which has the following properties:

$$\zeta(x) = -i\int_0^\infty e^{ixt}\,dt = \lim_{\alpha\to 0}\frac{1}{x+i\alpha},$$

$$= \lim_{t\to 0}\frac{1-e^{ixt}}{x},$$

$$= \mathcal{P}\left(\frac{1}{x}\right) - i\pi\,\delta(x), \tag{2-28}$$

$$x\,\zeta(x) = 1,$$

$$\int_{-\infty}^{\infty}\zeta(x)\,e^{ixt}\,dx = \begin{cases} 0 & \text{for } t>0 \\ -2\pi i & \text{for } t<0 \end{cases} \tag{2-29}$$

and

$$\lim_{t\to\infty}\zeta(x)\,e^{\pm ixt} = \begin{cases} 0 \\ -2\pi i\,\delta(x) \end{cases}. \tag{2-30}$$

In Eq.(2-28), $\mathcal{P}(1/x)$ is the principal value of $1/x$, which behaves like $1/x$ everywhere where $x \neq 0$ and vanishes at $x = 0$.

By substituting $G_f(E)$ from Eq.(2-27) into Eq.(2-23) and Eq.(2-24), one obtains the following equations

$$(E-E_i' + i/2\,\gamma_{ii})\,G_i(E) = H_{io}G_o(E) + V_{ab}G_j(E) - i/2\,\gamma_{ij}\,G_j(E) \tag{2-31}$$

$$(E-E_j' + i/2\,\gamma_{jj})\,G_j(E) = H_{jo}G_o(E) + V_{ba}G_i(E) - i/2\,\gamma_{ji}\,G_i(E) \tag{2-32}$$

where

$$-\frac{i}{2}\Upsilon_{ij}(E) = \sum_f H_{if}H_{fj}\,\delta(E-E_f') \quad . \tag{2-33}$$

In Eq.(2-31) and Eq.(2-32), the state vectors for the absorbed radiation field are the same in the two states $|i\rangle$ and $|j\rangle$ because the matrix element V_{ab} vanishes if $|i\rangle$ and $|j\rangle$ have different photons.

It can be shown that the Υ_{ij} for i ≠ j vanish whenever $|i\rangle$ and $|j\rangle$ are states of good angular momentum (9) {For a proof see Ref. (11)}. This is the case here and thus $\Upsilon_{ij} = 0$ for i ≠ j.

From Eq.(2-31) and Eq.(2-32), the following expressions for $G_i(E)$ and $G_j(E)$ are obtained:

$$G_i(E) = \frac{[H_{io}(E-E_j'+i\Upsilon_{jj}/2) + V_{ab}H_{jo}]\,G_o(E)}{(E-E_i'+i/2\,\Upsilon_{ii})(E-E_j'+i/2\,\Upsilon_{jj}) - |V_{ab}|^2}$$

$$G_j(E) = \frac{[H_{jo}(E-E_i'+i/2\,\Upsilon_{ii}) + V_{ba}H_{io}]\,G_o(E)}{(E-E_i'+i/2\,\Upsilon_{ii})(E-E_j'+i/2\,\Upsilon_{jj}) - |V_{ab}|^2} \quad . \tag{2-34}$$

These expressions are substituted in Eq.(2-22), which yields

$$G_o(E) = \frac{1}{E-E_o'+i/2\,\Gamma(E)} \tag{2-35}$$

where

$$-i/2\cdot\Gamma(E) = \sum_{k_\nu}[H_{oi}V_{ab}H_{jo} + H_{oj}V_{ba}H_{io}$$

$$+ |H_{oi}|^2(E-E_j'+i/2\,\Upsilon_{jj}) + |H_{oj}|^2(E-E_i'+i/2\,\Upsilon_{ii})]\times$$

$$[(E-E_i'+i/2\,\Upsilon_{ii})(E-E_j'+i/2\,\Upsilon_{jj}) - |V_{ab}|^2]^{-1} \quad . \tag{2-36}$$

The summation over k_r is over frequency, direction and polariztion of the incident radiation. The states $|i\rangle$ and $|j\rangle$ have the same absorbed photon $\vec{k}_r$.

Combining Eq.(2-34) and Eq.(2-35), one obtains

$$G_i(E) = \frac{H_{io}(E-E_j' + i/2\,\Upsilon_{jj}) + V_{ab}H_{jo}}{[(E-E_i'+i/2\,\Upsilon_{ii})(E-E_j'+i/2\,\Upsilon_{jj}) - |V_{ab}|^2][E-E_o'+i/2\,\Gamma]} \quad (2\text{-}37)$$

and

$$G_j(E) = \frac{H_{jo}(E-E_i' + i/2\,\Upsilon_{ii}) + V_{ba}H_{io}}{[(E-E_i'+i/2\,\Upsilon_{ii})(E-E_j'+i/2\,\Upsilon_{jj}) - |V_{ab}|^2][E-E_o'+i/2\,\Gamma]} . \quad (2\text{-}38)$$

B. <u>Determination of the Poles in G(E)</u>

The real parts of $\Upsilon_{ii}(E)$ and $\Upsilon_{jj}(E)$ have the following E dependence (see Appendix A-2):

$$Re\,(\Upsilon_{ii}(E)) = (E - E_c' + k_r)\,D_a$$

and (2-39)

$$Re\,(\Upsilon_{jj}(E)) = (E - E_c' + k_r)\,D_b$$

where D_a and D_b are defined in Eq.(A- 9) and Eq.(A-14).

In Appendix A-3, it is shown that the real part of Γ does not depend on E. Thus, absorbing the imaginary parts of Υ_{ii} , Υ_{jj} and Γ in the energies of the atomic states (see Appendix A-2), one can write the denominator of G(E) as

$$[\{E-E_i' + \tfrac{i}{2}Re(\Upsilon_{ii})\}\{E-E_j' + \tfrac{i}{2}Re(\Upsilon_{jj})\} - |V_{ab}|^2][E-E_o + i/2\,Re(\Gamma)] . \quad (2\text{-}40)$$

Substituting the real parts of γ_{ii} and γ_{jj} from Eq.(2-39) and replacing Re(Γ) by Γ , one gets

$$[\{E(1+iD_a/2)-E_i' + (k_r-E_c')iD_a/2\}\{E(1+iD_b/2)-E_j'$$

$$+(k_r-E_c')iD_b/2\} - |V_{ab}|^2].[E-E_o'+i\Gamma/2] \ . \qquad (2\text{-}41)$$

Combining Eq.(2-18), Eq.(2-26) and Eq.(2-41) and rearranging the terms, one can write the denominator of G(E) as

$$(1+iD_a/2)(1+iD_b/2)[\{E+k_r-\frac{E_a'(1-iD_a/2)}{1+D_a^2/4}-\frac{E_c'D_a^2}{4(1+D_a^2/4)}$$

$$-i\frac{E_c'D_a}{2}\}\{E+k_r-\frac{E_b'(1-iD_b/2)}{1+D_b^2/4}-\frac{E_c'D_b^2}{4(1+D_b^2/4)}-iE_c'D_b/2\}$$

$$-|V_{ab}|^2\cdot\{1-D_aD_b/4-i(D_a+D_b)\}/\{(1+D_a^2/4)(1+D_b^2/4)\}]\times[E-E_c'+i\Gamma/2] \ .$$

Since D_a and D_b are very small (see Eq.(A-13)), one can neglect the terms $D_a^2/4$, $D_b^2/4$ and $D_aD_b/4$ compared to unity and one gets

$$(1+iD_a/2)(1+iD_b/2)[\{E-E_a'+k_r-E_c'D_a^2/4+i\gamma_a/2\}\times\{E-E_b'+k_r$$

$$-\frac{E_c'D_b^2}{4}+i\gamma_b/2\}-|V_{ab}|^2\{1-i(D_a+D_b)\}][E-E_c'+i\Gamma/2] \quad (2\text{-}42)$$

where

$$\gamma_a = (E_a'-E_c')D_a$$

and (2-43)

$$\gamma_b = (E_b'-E_c')D_b \ .$$

It is shown in Chapter III that γ_a and γ_b as defined in Eq.(2-43) are the decay constants of the unperturbed atomic states $|a\rangle$ and $|b\rangle$, respectively. It is worth mentioning here that γ_a and γ_b are the real parts of $\gamma_{ii}(E)$ and $\gamma_{jj}(E)$ evaluated at E equal to E_i' and E_j', respectively.

Combining Eq.(2-37) to Eq.(2-39), Eq.(2-42) and Eq.(2-43), one gets

$$G_i(E) = [H_{io}(E - E_b' - E_c' D_b^2/4 + k_r) + V_{ab} H_{jo} + i/2 (H_{io}\gamma_b - V_{ab} H_{jo} D_b)]$$
$$\times[[(E - E_a' - E_c' D_a^2/4 + k_r + i\gamma_a/2)(E - E_b' - E_c' D_b^2/4 + k_r + i\gamma_b/2)$$
$$- |V_{ab}|^2(1 - i(D_a + D_b)/2)].(1 + i D_a/2)(E - E_c' + i\Gamma/2)]^{-1} \quad (2\text{-}44)$$

and

$$G_j(E) = [H_{jo}(E - E_a' - E_c' D_a^2/4 + k_r) + V_{ba} H_{io} + i/2 (H_{jo}\gamma_a - V_{ba} H_{io} D_a)]$$
$$\times[[(E - E_a' - E_c' D_a^2/4 + k_r + i\gamma_a/2)(E - E_b' - E_c' D_b^2/4 + i\gamma_b/2)$$
$$- |V_{ab}|^2\{1 - i(D_a + D_b)/2\}](1 + i D_b/2).(E - E_c' + i\Gamma/2)]^{-1}. \quad (2\text{-}45)$$

Since the matrix elements H_{jo} and V_{ab} are of the order of H_{io} and γ_b, respectively, and since $D_b \sim 10^{-10}$ (See Appendix A-2), the second term in $(H_{io}\gamma_b - V_{ab}H_{jo}D_b)$ can be neglected compared to the first one. Thus one can set

$$H_{io}\gamma_b - V_{ab} H_{jo} D_b \simeq H_{io}\gamma_b \quad (2\text{-}46)$$

and by similar arguments

$$H_{jo}\Upsilon_a - V_{ba} H_{io} D_a \simeq H_{jo}\Upsilon_a \quad . \tag{2-47}$$

Similarly in Eq.(2-44) and Eq.(2-45), the terms $E_c' D_a^2/4$ and $E_c' D_b^2/4$ are also very small compared to the other terms and therefore can be neglected without significant error. Thus one gets

$$\begin{aligned} G_i(E) = {} & [\, H_{io}(E - E_b' + k_r) + V_{ab} H_{jo} + i/2\, H_{io}\Upsilon_b \,] / [\, \{(E - E_a' \\ & + k_r + i\Upsilon_a/2)(E - E_b' + k_r + i\Upsilon_b/2) - |V_{ab}|^2 (1 - i(D_a + D_b)/2)\} \\ & \times (1 + iD_a/2)(E - E_c' + i\Gamma/2)\,] \\ G_j(E) = {} & [\, H_{jo}(E - E_a' + k_r) + V_{ba} H_{io} + i H_{jo}\Upsilon_a/2 \,] / [\, \{(E - E_a' \\ & + k_r + i\Upsilon_a/2)(E - E_b' + k_r + i\Upsilon_b/2) - |V_{ab}|^2 (1 - i(D_a + D_b)/2)\} \\ & \times (1 + iD_b/2)(E - E_c' + i\Gamma/2)\,] \; . \end{aligned} \tag{2-48}$$

The Fourier coefficients $G_i(E)$ and $G_j(E)$ have three poles. The first two poles are obtained from the roots of the equation

$$(E - E_a' + k_r + i\Upsilon_a/2)(E - E_b' + k_r + i\Upsilon_b/2) - |V_{ab}|^2 \{1 - i(D_a + D_b)/2\} = 0 \tag{2-49}$$

and the third pole is at

$$E_3' = E_c' - i\Gamma/2 \quad . \tag{2-50}$$

The roots of Eq.(2-49) are obtained by the method discussed in Appendix A-3. The result is

$$\left.\begin{matrix} E_1' \\ E_2' \end{matrix}\right\} = \frac{E_a' + E_b'}{2} - k_r \pm R - i(x_3 \pm I) \qquad (2\text{-}51)$$

where X_3, R and I are defined in Eq.(A-26) and Eq.(A-27).

C. Evaluation of the Probability Amplitudes

The probability amplitude $b_n(t)$ is calculated by evaluating the integral

$$b_n(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} G_n(E)\, e^{i(E_n - E)t}\, .dE$$

by contour integration.

Thus, using the expressions for $G_n(E)$ from Eq.(2-27), Eq.(2-35), Eq.(2-37), and Eq.(2-38), one gets the following integrals for the $b_n(t)$:

$$b_o(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, \frac{e^{i(E_o - E)t}}{(E - E_3')} \quad ,$$

$$b_i(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, \frac{H_{io}(E - E_j' + i/_2\Gamma_b) + V_{ab} H_{jo}}{(1 + iD_a/2)(E - E_1')(E - E_2')(E - E_3')}\cdot e^{i(E_i - E)t}$$

$$b_j(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, \frac{H_{jo}(E - E_i' + i/_2\Gamma_a) + V_{ba} H_{io}}{(1 + iD_b/2)(E - E_2')(E - E_1')(E - E_3')}\cdot e^{i(E_j - E)t}$$

(2-52)

and

$$b_f(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE \, \zeta(E-E_f')\left[H_{fi}\left(H_{io}(E-E_j'+i/2\,\Upsilon_b)+V_{ab}H_{jo}\right)\times\right.$$

$$\left.(1+iD_a/2)^{-1} + H_{fj}\left(H_{jo}(E-E_i'+i/2\,\Upsilon_a)+V_{ba}H_{io}\right)(1+iD_b/2)\right]$$

$$\times\left[(E-E_1')(E-E_2')(E-E_3')\right]^{-1}\cdot e^{i(E_f-E)t} \qquad (2\text{-}53)$$

where E_1', E_2' and E_3' are defined in Eq.(2-50) and Eq.(2-51).

The factors $(1+iD_a/2)$ and $(1+iD_b/2)$ in the probability amplitudes $b_i(t)$ and $b_j(t)$ go to unity when their modulus square is taken ($D_a \ll 1$ and $D_b \ll 1$).

Since the imaginary parts of the poles are negative, the path of integration in the integrals in Eq.(2-52) and Eq.(2-53)is taken to be a clockwise infinite semicircular contour in the lower half of the complex plane. In the case of $b_o(t)$, $b_i(t)$ and $b_j(t)$ all the poles lie in the lower half of the complex plane and thus, they all contribute to the integral. Thus using the method of residues, one gets

$$b_o(t) = e^{-iV_{cc}t - \Gamma t/2} \qquad (2\text{-}54)$$

$$b_i(t) = \frac{H_{io}(E_1'-E_j'+i/2\,\Upsilon_b)+V_{ab}H_{jo}}{(E_1'-E_2')(E_1'-E_3')}\cdot e^{i(E_i-E_1')t}$$

$$+\frac{H_{io}(E_2'-E_j'+i/2\,\Upsilon_b)+V_{ab}H_{jo}}{(E_2'-E_1')(E_2'-E_3')}\cdot e^{i(E_i-E_2')t}$$

$$+\ \frac{H_{io}\,(E_3' - E_j' + i\Gamma_b/2) + V_{ab}\,H_{jo}}{(E_3' - E_1')(E_3' - E_2')}\cdot e^{i(E_i - E_3')t} \tag{2-55}$$

and

$$b_j(t) = \frac{H_{jo}\,(E_1' - E_i' + i\Gamma_a/2) + V_{ba}\,H_{io}}{(E_1' - E_2')(E_1' - E_3')}\cdot e^{i(E_j - E_1')t}$$

$$+\ \frac{H_{jo}\,(E_2' - E_i' + i\Gamma_a/2) + V_{ba}\,H_{io}}{(E_2' - E_1')(E_2' - E_3')}\cdot e^{i(E_j - E_2')t}$$

$$+\ \frac{H_{jo}\,(E_3' - E_i' + i\Gamma_a/2) + V_{ba}\,H_{io}}{(E_3' - E_1')(E_3' - E_2')}\cdot e^{i(E_j - E_3')t} \tag{2-56}$$

The Zeta function $\zeta(E-E_f')$ in the integral in Eq.(2-53) makes the path of integration along the real axis to go arround a semicircle of infinitely small radius, in the upper half of the complex plane, centered at $E = E_f'$ (see Fig.2-1). The remaining path of integration is the same as in the previous cases.

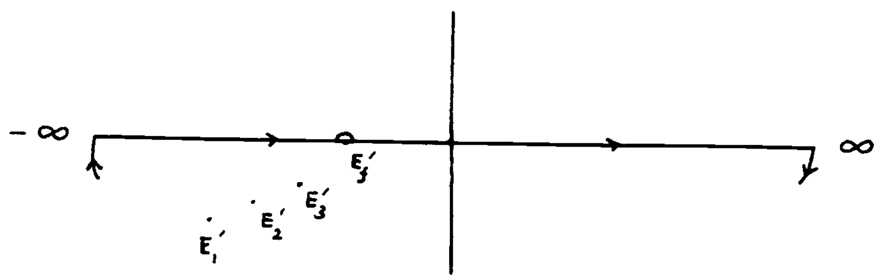

Fig. 2-1. Position of poles in the complex plane

Thus, using the method of residues, Eq.(2-53) gives

$$
\begin{aligned}
b_f(t) = {} & [\, H_{fi} \{ H_{io} (E_f' - E_j' + i\gamma_b/2) + V_{ab} H_{jo} \} \\
& + H_{fj} \{ H_{jo} (E_f' - E_i' + i\gamma_a/2) + V_{ba} H_{io} \}] \\
& \times [(E_f' - E_1')(E_f' - E_2')(E_f' - E_3')]^{-1} \cdot e^{-iV_{cc}t} \\
& + [H_{fi} \{ H_{io} (E_1' - E_j' + i\gamma_b/2) + V_{ab} H_{jo} \} \\
& + H_{fj} \{ H_{jo} (E_1' - E_i' + i\gamma_a/2) + V_{ba} H_{io} \}] \\
& \times [(E_1' - E_f')(E_1' - E_2')(E_1' - E_3')]^{-1} e^{i(E_f - E_1')t} \\
& + [H_{fi} (H_{io} (E_2' - E_j' + i\gamma_b/2) + V_{ab} H_{jo}) \\
& + H_{fj} \{ H_{jo} (E_2' - E_i' + i\gamma_a/2) + V_{ba} H_{io} \}] \\
& \times [(E_2' - E_f')(E_2' - E_1')(E_2' - E_3')]^{-1} e^{i(E_f - E_2')t} \\
& + [H_{fi} \{ H_{io} (E_3' - E_j' + i\gamma_b/2) + V_{ab} H_{jo} \} \\
& + H_{fj} \{ H_{jo} (E_3' - E_i' + i\gamma_a/2) + V_{ba} H_{io} \}] \\
& \times [(E_3' - E_f')(E_3' - E_1')(E_3' - E_2')]^{-1} e^{i(E_f - E_3')t} \, .
\end{aligned}
\qquad (2\text{-}57)
$$

From Eq.(2-54), it is seen that the probability $b_o(t)$ decays monotonically with a single decay constant Γ.

The probability amplitudes $b_i(t)$ and $b_j(t)$ have three terms. Each term has two time dependent factors, one is oscillatory and the other is exponentially decaying. The oscillatory behaviour depends on the frequencies of emitted and absorbed radiations, the coupling strength of the external perturbation and the energy difference between the two excited states. The coupling strength and the energy difference also affect the decay constants of $b_i(t)$ and $b_j(t)$.

The amplitude of the final states, $b_f(t)$ in Eq.(2-57) has four terms. The first term is pure oscillatory in time and the other three terms have an oscillatory and an exponentially decaying factors with different oscillatory frequency and decay constant. The decay constants are the same as the ones in $b_i(t)$ and $b_j(t)$.

As $t \to \infty$, only the first term in $b_f(t)$ survives and all other probability amplitudes decay to zero.

Thus

$$b_f(t\to\infty) = \left[H_{fi}\left\{H_{io}(E_f'-E_j'+i\gamma_b/2)+V_{ab}H_{jo}\right\}+H_{fj}\left\{H_{jo}(E_f'-E_i'+i\gamma_a/2)\right.\right.$$

$$\left.\left.+V_{ba}H_{io}\right\}\right]\times\left[(E_f'-E_1')(E_f'-E_2')(E_f-E_3')\right]^{-1}\cdot e^{-iV_{cc}t} \qquad (2\text{-}58)$$

This gives the probability amplitude for the process where the atom absorbs a photon with wave vector $\vec{k}_\mu$ and polarization $\hat{e}_\mu$ and emits a photon with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$.

The probability of emission of a photon with wave vector $\vec{k}_\lambda$ and polarization $\vec{e}_\lambda$ is obtained by summing over the incident frequencies:

$$P(\hat{e}_\sigma, k_\lambda) = \sum_{k_\sigma} |b_f(\infty)|^2 \quad . \tag{2-59}$$

The summation over k_σ is over the frequency of the absorbed photons only. The symbol k_λ in the parenthesis stands for the frequency, direction and polarization of the scattered beam and $\hat{e}_\sigma$ stands for the direction and polarization of the incident beam.

For a continuous distribution of incident frequencies, the $P(\hat{e}_\sigma, k_\lambda)$ is given by (see Appendix B-1)

$$\begin{aligned}
P(\hat{e}_\sigma, k_\lambda) = {} & e^4 I_0/(L^3 \Gamma k_0^3) \cdot [\{(K+\Delta/2)^2 + \gamma_b^2/4\} |p_{ca}^\lambda|^2 \cdot |p_{ac}^\sigma|^2 \\
& + \{(K-\Delta/2)^2 + \gamma_a^2/4\} |p_{cb}^\lambda|^2 \cdot |p_{bc}^\sigma|^2 + V^2 \{|p_{ca}^\lambda|^2 |p_{bc}^\sigma|^2 + |p_{cb}^\lambda|^2 \cdot |p_{ac}^\sigma|^2 \\
& + 4\,\mathrm{Re}(p_{ca}^\lambda p_{cb}^{\lambda *})\,\mathrm{Re}(p_{ac}^\sigma p_{bc}^{\sigma *}) - 2\,\mathrm{Re}(p_{ca}^\lambda p_{cb}^{\lambda *} p_{ac}^\sigma p_{bc}^{\sigma *})\} \\
& + 2V[\{(K+\Delta/2)|p_{ca}^\lambda|^2 + (K-\Delta/2)|p_{cb}^\lambda|^2\}\,\mathrm{Re}(p_{ac}^\sigma p_{bc}^{\sigma *}) \\
& \quad + \{(K+\Delta/2)|p_{ac}^\sigma|^2 + (K-\Delta/2)|p_{bc}^\sigma|^2\}\,\mathrm{Re}(p_{ca}^\lambda p_{cb}^{\lambda *}) \\
& \qquad + (\gamma_a |p_{cb}^\lambda|^2 - \gamma_b |p_{ca}^\lambda|^2)\,\tfrac{1}{2}\,\mathrm{Im}(p_{ac}^\sigma p_{bc}^{\sigma *}) \\
& \qquad + (\gamma_a |p_{bc}^\sigma|^2 - \gamma_b |p_{ac}^\sigma|^2)\,\tfrac{1}{2} \cdot \mathrm{Im}(p_{ca}^\lambda p_{cb}^{\lambda *}) \\
& \quad + \{(K-\Delta/2)(K+\Delta/2) + \gamma_a\gamma_b/4\} \cdot 2 \cdot \mathrm{Re}(p_{ca}^\lambda p_{cb}^{\lambda *} p_{ac}^\sigma p_{bc}^{\sigma *}) \\
& \quad + \{\gamma_a(K+\Delta/2) - \gamma_b(K-\Delta/2)\}\,\mathrm{Im}(p_{ca}^\lambda p_{cb}^{\lambda *} p_{ac}^\sigma p_{bc}^{\sigma *})] \\
& \quad \times [(K-\Delta/2)^2 \{(K+\Delta/2)^2 + \gamma_b^2/4\} + (K+\Delta/2)^2 \gamma_a^2/4 \\
& \quad - 2V^2 (K-\Delta/2)(K+\Delta/2) + (V^2 + \gamma_a\gamma_b/4)^2]^{-1}
\end{aligned} \tag{2-60}$$

This expression has in general two peaks. The lineshapes and linewidths depend on the external coupling strength, the energy separation of the excited states and the decay constants of the excited states. In the case, where one of the decay constants is zero, a hole is observed in the frequency spectrum of $P(\hat{e}_\sigma, k_\lambda)$ at the frequency equal to the frequency difference of the ground state and non-decaying unperturbed excited state. A detail analysis of $P(\hat{e}_\sigma, k_\lambda)$ is presented in Chapter III for some special cases.

D. Intensity of Scattered Radiation in a Given Direction with Definite Polarization

For a beam of incident radiation with polarization σ and direction (θ_a, ϕ_a), the intensity of the scattered radiation, $I(\Omega_a, \Omega_e, \sigma, \lambda)$ with polarization λ and direction (θ_e, ϕ_e) is obtained by integrating the probability $P(\hat{e}_\sigma, k_\lambda)$ over the frequency k_λ:

$$I(\Omega_a, \Omega_e, \sigma, \lambda) = L^3/(2\pi)^3 \cdot \int_0^\infty P(\hat{e}_\sigma, k_\lambda)\, k_\lambda^2\, dk_\lambda \tag{2-61}$$

where Ω_a and Ω_e indicate the directions; and σ and λ the polarizations of the incident and the emitted radiation fields, respectively. This integral is evaluated in Appendix B-2. The result is

$$I(\Omega_a, \Omega_e, \sigma, \lambda) = \frac{e^4 I_0}{8\pi^2 \Gamma k_0} \cdot \Big[\frac{|P_{ca}^{\lambda}|^2 |P_{ac}^{\sigma}|^2}{x_a} + \frac{|P_{cb}^{\lambda}|^2 |P_{bc}^{\sigma}|^2}{x_b}$$

$$+\Big[V^2 (x_a+x_b)\, x_a x_b \Big\{ \frac{4\,Re(P^{\lambda}_{ca} P^{\lambda *}_{cb})\, Re(P^{\sigma}_{ac} P^{\sigma *}_{bc})}{x_a x_b}$$

$$-\,(|P^{\lambda}_{ca}|/x_a - |P^{\lambda}_{cb}|^2/x_b)(|P^{\sigma}_{ac}|^2/x_a - |P^{\sigma}_{bc}|^2/x_b)\Big\}$$

$$+\,V(x_a+x_b)\big[\Delta \{ (|P^{\lambda}_{ca}|^2 - |P^{\lambda}_{cb}|^2)\, Re(P^{\sigma}_{ac} P^{\sigma *}_{bc}) + (|P^{\sigma}_{ac}|^2 - |P^{\sigma}_{bc}|^2)\, Re(P^{\lambda}_{ca} P^{\lambda *}_{cb}) \}$$

$$-\,2\{ (|P^{\lambda}_{ca}|^2 x_b - |P^{\lambda}_{cb}|^2 x_a)\, Im(P^{\sigma}_{ac} P^{\sigma *}_{bc}) + (|P^{\sigma}_{ac}|^2 x_b - |P^{\sigma}_{bc}|^2 x_a)\, Im(P^{\lambda}_{ca} P^{\lambda *}_{cb}) \}\big]$$

$$+\,4 x_a x_b (x_a+x_b)\, Re(P^{\lambda}_{ca} P^{\lambda *}_{cb} P^{\sigma}_{ac} P^{\sigma *}_{bc})$$

$$+\,4 x_a x_b \Delta\, Im(P^{\lambda}_{ca} P^{\lambda *}_{cb} P^{\sigma}_{ac} P^{\sigma *}_{bc}) \Big] \times$$

$$\big[(x_a+x_b)^2 (V^2 + x_a x_b) + \Delta^2 x_a x_b \big]^{-1} \qquad (2\text{-}62)$$

The first two terms are constants. They arise from the direct resonance fluorescence process of the two uncoupled states. The next six terms are due to the presence of an off diagonal matrix element V_{ab} of the external perturbation. These terms are called "Anticrossing - signals". The name "Anticrossing" is given because the perturbed energy levels of the two excited states repel each other when plotted as a function of the external perturbation. The last two terms are "Crossing signals". The name "crossing" arises from the fact that the perturbed energy levels of the two excited states cross each other when plotted as a function of the external perturbation.

The Anticrossing and Crossing signals disappear if one of the excited states is non-decaying. As a function of the energy separation Δ, the crossing signal has two terms; one is Lorentzian and the other is dispersion. The crossing signal will be pure Lorentzian or dispersion depending on whether $P^{\lambda}_{ca} P^{\lambda *}_{cb} P^{\mu}_{ac} P^{\mu *}_{bc}$ is a real or imaginary quantity, respectively.

As an application, the intensity $I(\Omega_a, \Omega_e, \mu, \lambda)$ for the 2^2P states of Li^7 is calculated in Chapter IV.

III. RESONANCE FLUORESCENCE WITH ONE DECAYING AND ONE NON-DECAYING STATES

The theory developed in Chapter II is used here to discuss the resonance scattering of radiation from an atomic system where only one of the excited states is decaying. The atomic state $|b\rangle$ is considered to be the non-decaying state ($\gamma_b = 0$).

In general, the energies of the excited states obtained from the real parts of the poles of G(E) are different from the energies obtained without considering the radiation interaction (16). A detail discussion of these energies is presented in the next section. In the special case where the two excited states decay with the same rate, the energies obtained by the two different methods are the same. Hence, here the radiation interaction has no effect on the energy levels.

A. Discussion of E_1 and E_2

The real parts of the poles E_1 and E_2 of G(E) (see Chapter II-B) give the energies of the system when the atom is in an excited state. From Eq.(2-51), these energies are

$$\left.\begin{matrix} Re(E_1') \\ Re(E_2') \end{matrix}\right\} = (E_a' + E_b')/2 \pm [\{(\Delta^2 - X^2 + 4V^2)^2 + 4X^2\Delta^2\}^{1/2} + \Delta^2 - X^2 + 4V^2]^{1/2} \cdot 1/2\sqrt{2} - k_r \tag{3-1}$$

where Δ , X and V are defined in Eq.(A-23) and Eq.(A-27).

The energy $-k_r$ is the energy of the absorbed photon. The energies of the excited states of the atom are obtained by dropping the term $-k_r$ in Eq.(3-1). Thus,

$$\left.\begin{matrix} E_1 \\ E_2 \end{matrix}\right\} = (E_a'+E_b')/2 \pm \Big[\{ (\Delta^2 - X^2 + 4V^2)^2 + 4X^2\Delta^2 \}^{1/2} + \Delta^2 - X^2 + 4V^2 \Big]^{1/2} \cdot 1/2\sqrt{2} \quad . \tag{3-2}$$

If one does not take into account the radiation interaction, then the energies of the excited states become

$$\left.\begin{matrix} E_1^0 \\ E_2^0 \end{matrix}\right\} = (E_a'+E_b')/2 \pm \sqrt{\Delta^2+4V^2}\,/2 \quad . \tag{3-3}$$

This result has been obtained by diagonalising the Hamiltonian of the atom (see Appendix C).

Comparing Eq.(3-2) with Eq.(3-3), one finds that the energies E_1 and E_2 are different from the energies E_1^0 and E_2^0 provided $X \neq 0$. But for $X = 0$, Eq.(3-2) reduces to Eq.(3-3). This mean that the radiation interaction has no effect on the energy levels if the two excited states decay with the same decay rates.

For the case where the excited states are degenerate $(\Delta = 0)$ and $X \neq 0$, then Eq.(3-2) reduces to

$$\left.\begin{matrix} E_1 \\ E_2 \end{matrix}\right\} = (E_a'+E_b')/2 \pm \sqrt{4V^2 - X^2}\,/2 \tag{3-4}$$

and Eq.(3-3) becomes

$$\left.\begin{matrix} E_1^0 \\ E_2^0 \end{matrix}\right\} = (E_a'+E_b')/2 \pm V \quad . \tag{3-5}$$

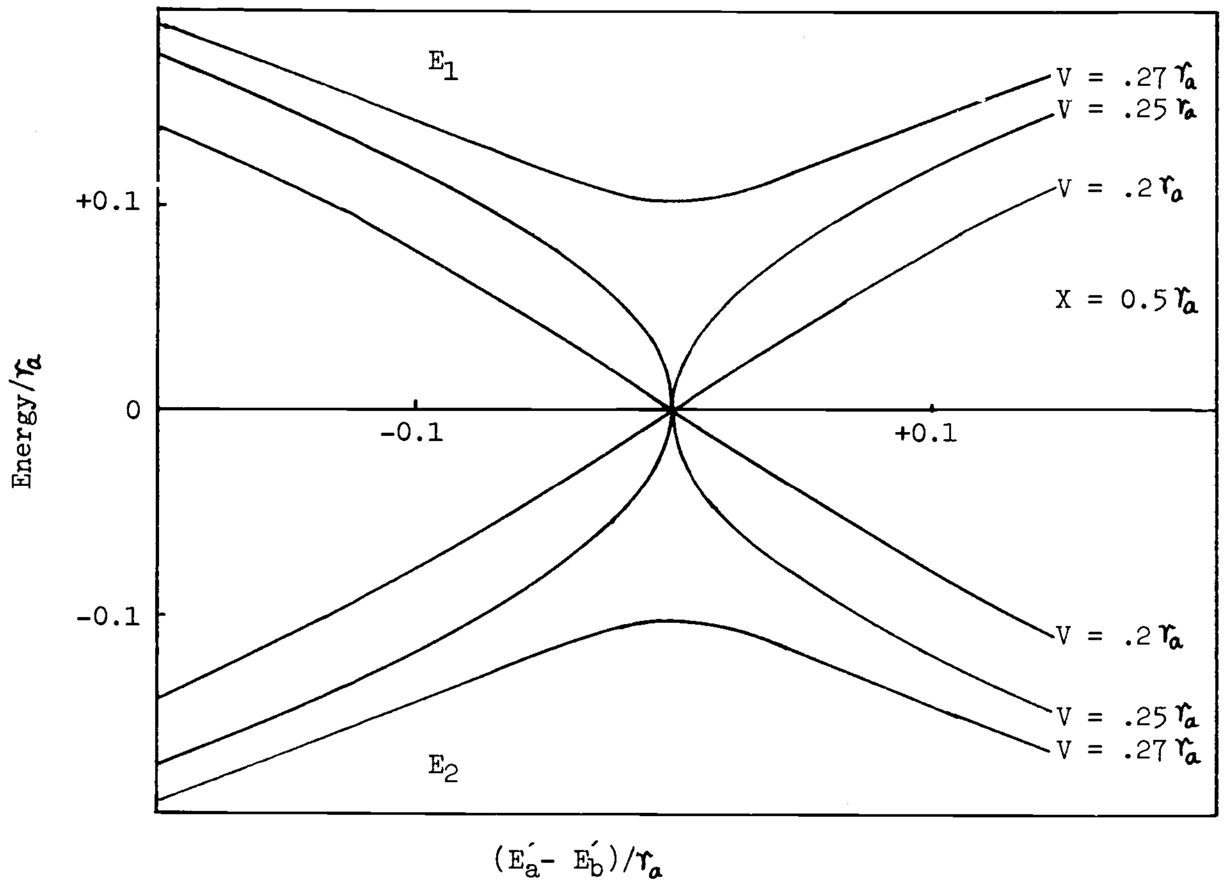

Fig. 3-1. Energies E_1 and E_2 as a function of the energy separation $(E_a' - E_b')$. The origin on the ordinate is set at $(E_a' + E_b')/2$.

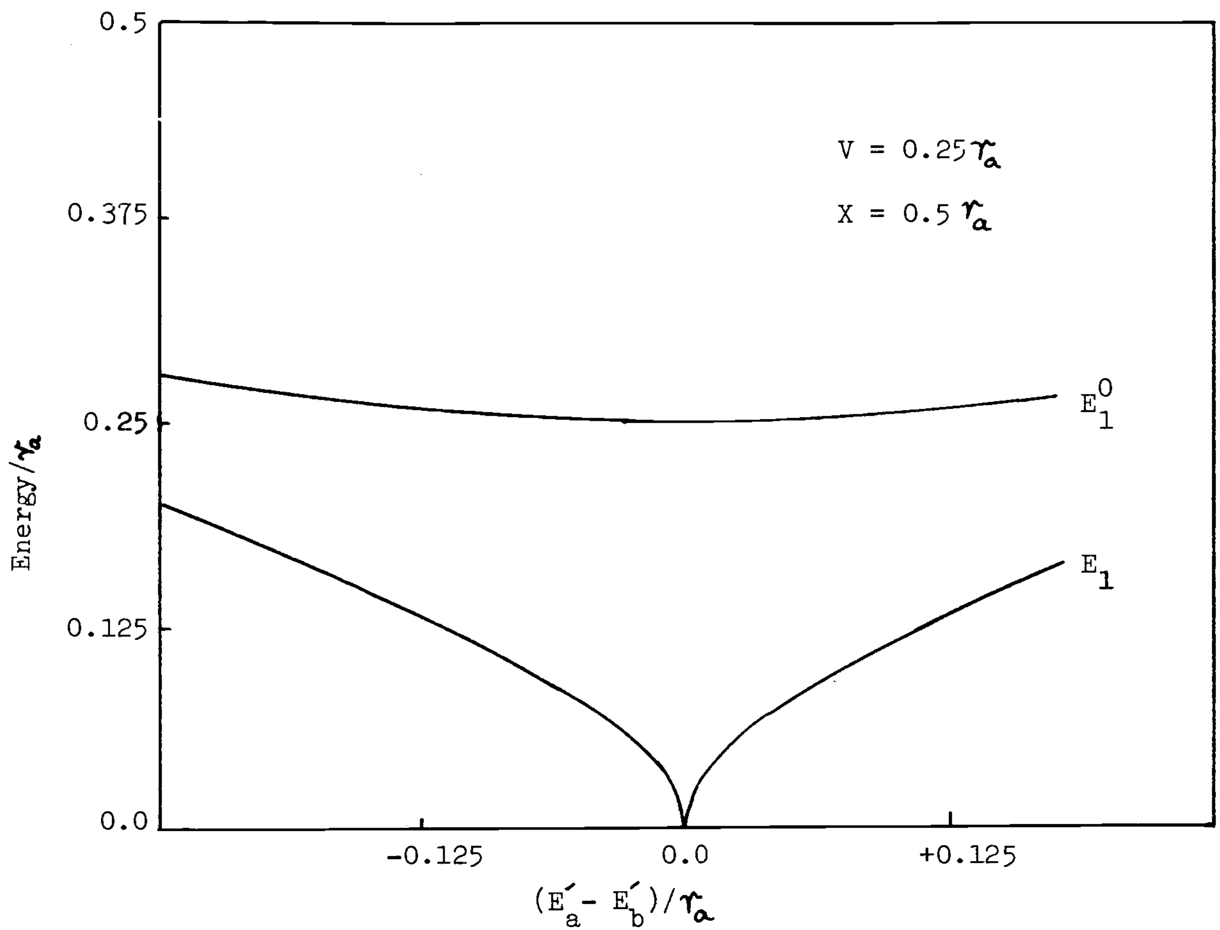

Fig. 3-2. Energies E_1 and E_1^0 as a function of the energy separation $(E_a' - E_b')$. The origin on the ordinate is set at $(E_a' + E_b')/2$.

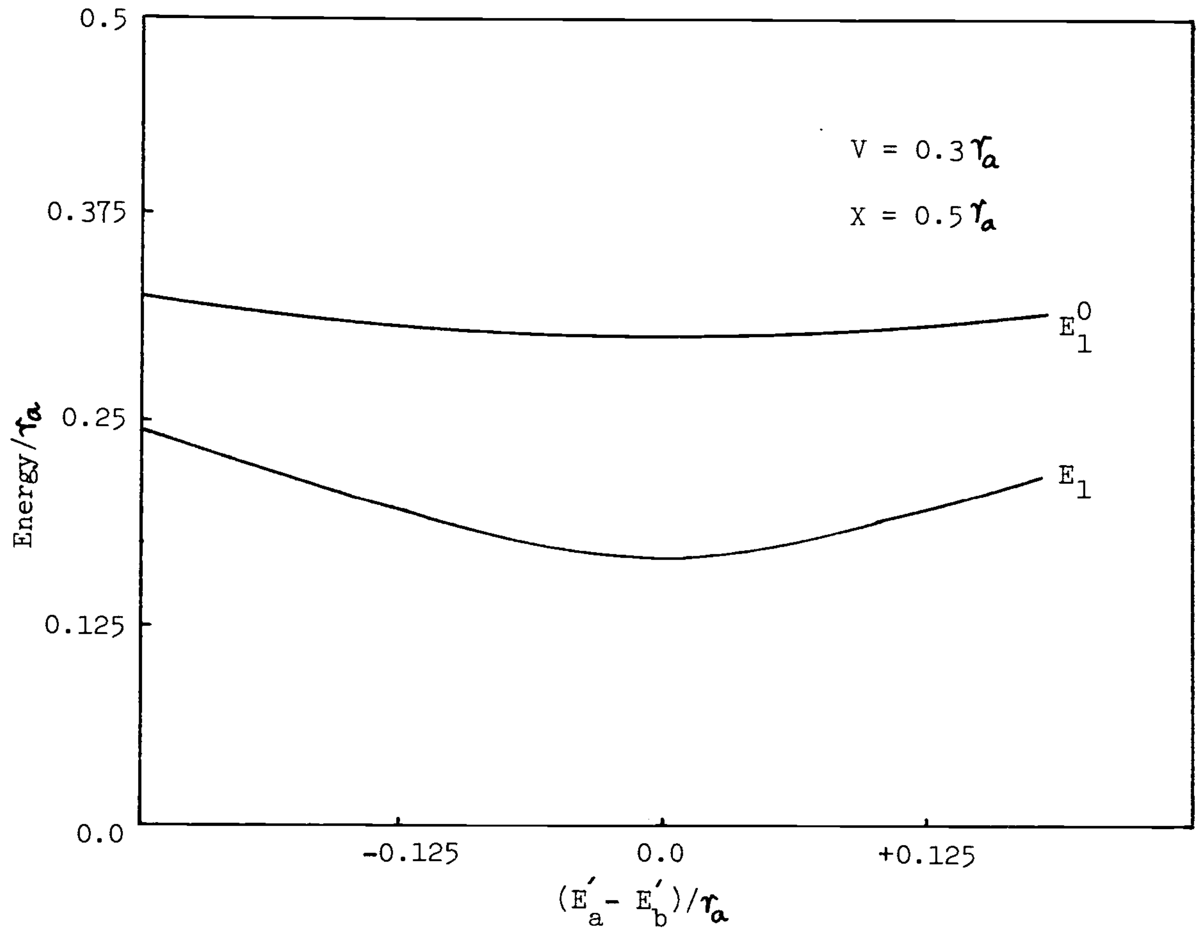

Fig. 3-3. Energies E_1 and E_1^0 as a function of the energy separation $(E_a' - E_b')$. The origin on the ordinate is set at $(E_a' + E_b')/2$.

Equation (3-4) shows that the energies E_1 and E_2 are degenerate if $4V^2 << X^2$, because in this case the term within the square root sign is either zero or imaginary (The imaginary part of the energies contribute to the decay rates of the excited states). For $4V^2 > X^2$, the two energies are non-degenerate and separated by an energy difference of $\sqrt{4V^2 - X^2}$. On the other hand if one neglects the radiation interaction, one finds that the external perturbation always removes the degeneracy and the two levels are separated by an energy difference of 2V{see Eq.(3-5)}.

The energies E_1 and E_2 are plotted in Fig.3-1 as a function of the energy difference Δ for different V. The value of X is taken to be $\gamma_a/2$. For $V \leq .25\gamma_a$ ($4V^2 \leq X^2$), one observes that the two energies approach each other and become degenerate for $\Delta = 0$. But for $V > .25\gamma_a$, the two energies are separated.

In Fig.3-2, the energies E_1 and E_1° are plotted as a function of Δ for $V = .25\gamma_a$ and $X = .5\gamma_a$ ($4V^2 = X^2$). The energy E_1 differes from E_1° significantely in the visinity of $\Delta = 0$. At large values of Δ , E_1 approches E_1° assymptotically. In Fig.3-3, similar graphs are plotted for $V = .3\gamma_a$ and $X = .5\gamma_a$ ($4V^2 > X^2$). In this case, the energy difference, ($E_1^\circ - E_1$) decreases as V increases.

B. Probability Amplitudes in Time and Frequency

For this special case where the state $|b\rangle$ is not decaying, the probability amplitudes are obtained from Eq.(2-54) to Eq.(2-57) by setting γ_b , H_{jo} and H_{fj} equal to zero. The results are:

$$b_o(t) = e^{-iV_{cc}t - \Gamma t/2} , \tag{3-6}$$

$$\begin{aligned} b_i(t) = &\frac{H_{io}(E_1' - E_j')\, e^{i(E_i - E_1')t}}{(E_1' - E_3')(E_1' - E_2')} \\ &+ \frac{H_{io}(E_2' - E_j')\, e^{i(E_i - E_2')t}}{(E_2' - E_3')(E_2' - E_1')} \\ &+ \frac{H_{io}(E_3' - E_j')\, e^{i(E_i - E_3')t}}{(E_3' - E_1')(E_3' - E_2')} , \end{aligned} \tag{3-7}$$

$$\begin{aligned} b_j(t) = &\frac{V_{ab}^{*} H_{io}}{(E_1' - E_2')} \left[\frac{e^{i(E_j - E_1')t}}{(E_1' - E_3')} - \frac{e^{i(E_j - E_2')t}}{(E_2' - E_3')} \right] \\ &+ \frac{V_{ba} H_{io}}{(E_3' - E_1')(E_3' - E_2')}\, e^{i(E_j - E_3')t} \end{aligned} \tag{3-8}$$

and

$$b_f(t) = \frac{H_{fi} H_{io}(E_f' - E_j')}{(E_f' - E_1')(E_f' - E_2')(E_f' - E_3')}\, e^{-iV_{cc}t}$$

$$+\frac{H_{fi}\,H_{io}\,(E_1'-E_j')}{(E_1'-E_f')(E_1'-E_2')(E_1'-E_3')}\cdot e^{i(E_f-E_1')t}$$

$$+\frac{H_{fi}\,H_{io}\,(E_2'-E_j')}{(E_2'-E_f')(E_2'-E_1')(E_2'-E_3')}\cdot e^{i(E_f-E_2')t}$$

$$+\frac{H_{fi}\,H_{io}\,(E_3'-E_j')}{(E_3'-E_f')(E_3'-E_1')(E_3'-E_2')}\cdot e^{i(E_f-E_3')t} \tag{3-9}$$

Substituting the expressions for E_f, E_f', E_1', E_2' and E_3' {see Eq.(2-18), Eq.(2-26) and Eq.(2-51)} into Eq.(3-7) to Eq.(3-9), one obtains:

$$b_i(t) = H_{io}\Big[\frac{\{R+\Delta/2-i(\gamma_a/4+I)\}\exp\{i(\Delta/2-R)t-(\gamma_a/4+I)t\}}{2(R-iI)[R-K_\alpha-i(\gamma_a/4+I-\Gamma/2)]}$$

$$+\frac{\{\Delta/2-R-i(\gamma_a/4-I)\}\exp\{i(\Delta/2+R)t-(\gamma_a/4-I)t\}}{2(R-iI)\,[R+K_\alpha+i(\gamma_a/4-I-\Gamma/2)]}$$

$$+\frac{\{K_\alpha+\Delta/2-i\Gamma/2\}\exp\{-i(K_\alpha-\Delta/2)t-\Gamma t/2\}}{[K_\alpha-R+i(\gamma_a/4+I-\Gamma/2)][K_\alpha+R+i(\gamma_a/4-I-\Gamma/2)]}\Big]\,. \tag{3-10}$$

$$b_j(t) = \frac{V_{ba}\,H_{io}}{2[R-iI]}\Big[\frac{\exp\{i(R-\Delta/2)t-(\gamma_a/4-I)t}{K_\alpha+R+i(\gamma_a/4-I-\Gamma/2)}$$

$$-\frac{\exp\{-i(R+\Delta/2)t-(\gamma_a/4+I)t\}}{K_\alpha-R+i(\gamma_a/4+I-\Gamma/2)}$$

$$+\frac{V_{ba}\,H_{io}\,\exp\{-i(K_\alpha+\Delta/2)t-\Gamma t/2\}}{[K_\alpha-R+i(\gamma_a/4+I-\Gamma/2)][K_\alpha+R+i(\gamma_a/4-I-\Gamma/2)]} \tag{3-11}$$

and

$$b_f(t) = \frac{H_{fi} H_{io} (K_\lambda + \Delta/2)}{[K_\lambda - K_\sigma + i\Gamma/2][K_\lambda - R + i(\gamma_a/4 + I)][K_\sigma + R - i(\gamma_a/4 - I)]}$$

$$+ \frac{H_{fi} H_{io} [R + \Delta/2 - i(\gamma_a/4 + I)] \exp\{i(K_\lambda - R)t - (\gamma_a/4 + I)t\}}{[K_\lambda - R + i(\gamma_a/4 + I)][K_\sigma - R + i(\gamma_a/4 + I - \Gamma/2)(R - iI).2}$$

$$+ \frac{H_{fi} H_{io} [R - \Delta/2 - i(\gamma_a/4 - I) \exp\{i(K_\lambda + R)t - (\gamma_a/4 - I)t\}}{[K_\lambda + R + i(\gamma_a/4 - I)][K_\sigma + R + i(\gamma_a/4 + I - \Gamma/2)][R - iI].2}$$

$$+ \frac{H_{fi} H_{io} [K_\sigma + \Delta/2 - i\Gamma/2] \exp\{-i(K_\sigma - K_\lambda)t - \Gamma t/2\}}{[K_\sigma - K_\lambda - i\Gamma/2][K_\sigma - R + i(\gamma_a/4 + I - \Gamma/2)][K_\sigma + R + i(\gamma_a/4 - I - \Gamma/2]} \qquad (3\text{-}12)$$

where

$$K_\sigma = k_\sigma - \frac{E_a' + E_b'}{2} + E_c' ,$$

$$K_\lambda = k_\lambda - \frac{E_a' + E_b'}{2} + E_c' ,$$

and R and I are defined in Eq.(A-27). The diagonal matrix elements V_{aa}, V_{bb} and V_{cc} are assumed to be zero in the expression for the probability amplitudes in Eq.(3-10) to Eq.(3-12). This assumption is true in most of the cases of practical interest.

From Eq.(3-6), one finds that the probability $|b_o(t)|^2$ of the ground state decays exponentially with a decay constant Γ.

The probability $|b_i(t)|^2$ gives the probability of the atom being in the excited state $|a\rangle$ with an absorbed photon with wave vector $\vec{k}_\sigma$. This probability has three pure decaying terms with decay constants $(\gamma_a/2 + 2I)$, $(\gamma_a/2 - 2I)$ and Γ and three oscillatory terms with decaying amplitudes. These oscillation frequencies are 2R, $K_\alpha + R$ and $K_\alpha - R$ and the decay constants of their amplitudes are $\gamma_a/2$, $(\gamma_a/4 - I + \Gamma/2)$ and $(\gamma_a/4 + I + \Gamma/2)$, respectively.

The probability $|b_i(t)|^2$ is plotted in Figs. 3-4 to 3-7 as a function of $K_\alpha \{K_\alpha = k_\alpha - (E_a + E_b)/2 + E_c\}$ for different times. At short times, this probability is small and quite broad but as the time increases, the probability narrows up into two peaks one near $K_\alpha = R$ and other near $K_\alpha = -R$. The peak near $K_\alpha = -R$ is weaker than the peak near $K_\alpha = R$. There are some wiggles on either sides of the peaks. These wiggles increase in number and become weaker as time increases. At short times, the hight of the peaks increases for some time and then starts decreasing at larger times and becomes zero $t = \infty$. An increase in V decreases the hight of the peak near $K_\alpha = R$ and increases the hight of the peak near $K_\alpha = -R$ (compare Fig. 3-6 and Fig. 3-8)). For V = 0, only one peak at $K_\alpha = R$ is obtained. A physical reason of these changes in the peak hights can be attributed to the fact that the decaying state $|a\rangle$ is coupled to the non-decaying state $|b\rangle$ through the coupling matrix element V and this coupling mixes the two states unequally for $\Delta \neq 0$. This means that the probability of the atom in state $|a\rangle$ is larger at the energy E_1 (the perturbed energy corresponding to E_a) than the probability at the energy E_2 (the perturbed energy corresponding to E_b). This explains that the peak near $K_\alpha = R$ (corresponding to E_1) is higher than the peak near $K_\alpha = -R$ (corresponding to E_2). As V increases, the probability of the atom in state $|a\rangle$ decreases at the energy E_1 and increases at energy E_2. This explains the change in the hights of the peaks with the change in V. For $\Delta = 0$, the two states are mixed equally and thus the two peaks in Fig. 3-10 have equal hights.

In Fig. 3-1o, the probability $|b_i(t)|^2$ is plotted as a function of time for different frequencies of the absorbed photons. At short times, all the three oscillation frequencies (2R, K_σ+ R and K_σ- R) contribute to the oscillations in $|b_i(t)|^2$ but at large times K_σ+ R is the dominant frequency because the term with this frequency dies out slowely copared to the orther terms. These frequencies depend on the relative positions of the two excited states and the frequency of the absorbed photon. A physical reason for these frequencies can be attributed to the radiation reaction on the basis of the following classical picture of the system. The atom which consists of two oscillators of frequencies $Re(E_1)-E_c'$ and $Re(E_2)-E_c'$ interacts with the radiation field of frequency k_σ through radiative coupling. This coupling produces three oscillation frequencies which are k_σ- $Re(E_1)$ $+E_c$, k_σ- $Re(E_2)$ + E_c and $Re(E_1 - E_2)$. These are the same frequencies which appear in the probability $|b_i(t)|^2$ $\{k_\sigma - Re(E_1)+ E_c = K - R;$ $k_\sigma - Re(E_2)+ E_c = K + R;$ $Re(E_1 - E_2)= 2R\}$. The decrease in the amplitudes of the oscillations can be attributed to the fact that the probability of the incident photon to exist without being absorbed decreases as time increases and it tends to zero as $t \to \infty$. Thus, there are no photons left to interact with the atom and therefore no wiggles appear in $|b_i(t)|^2$ at large times.

From Eq.(3-11), one finds that $|b_j(t)|^2$, the probability of the atom in the excited state $|b\rangle$ with an absorbed photon with wave vector k_α, has also three pure decaying terms and three oscillatory terms with decaying amplitudes. These oscillation frequencies and the decay constants are the same as those obtained in the case of $|b_i(t)|^2$. The probability $|b_j(t)|^2$ is plotted as a function of K_α and time t in Fig. 3-11 and Fig. 3-12, respectively. These plots have, in general, similar features as those of $|b_i(t)|^2$ as discussed earlier.

The probability $|b_f(t)|^2$ gives the probability of the atom in the state $|c\rangle$ with a photon of wave vector $\vec{k}_\alpha$ absorbed and a photon of wave vector k_λ emitted. This probability is plotted in Figs.3-13 to 3-16 as a function of the absorbed frequency k_α for a given emitted frequency k_λ and time t. One principal maximum is observed at $k_\alpha = k_\lambda$ with many secondary maxima. The principal maximum is wide for short times and narrowes up at large times. This means that the off channel $(k_\alpha \neq k_\lambda)$ scattering is quite significant at small times but becomes negligible at large times. As $t \to \infty$, the plot of $|b_f(t)|^2$ as a function of k_α becomes a Dirac delta function $\delta(k_\alpha - k_\alpha^0)$ {see Fig. 3-16}. As time increases, the number of secondary maxima increase and their amplitudes decrease. A physical reason for these secondary maxima can be attributed to the same reasoning as discussed in the case of $|b_i(t)|^2$, previously.

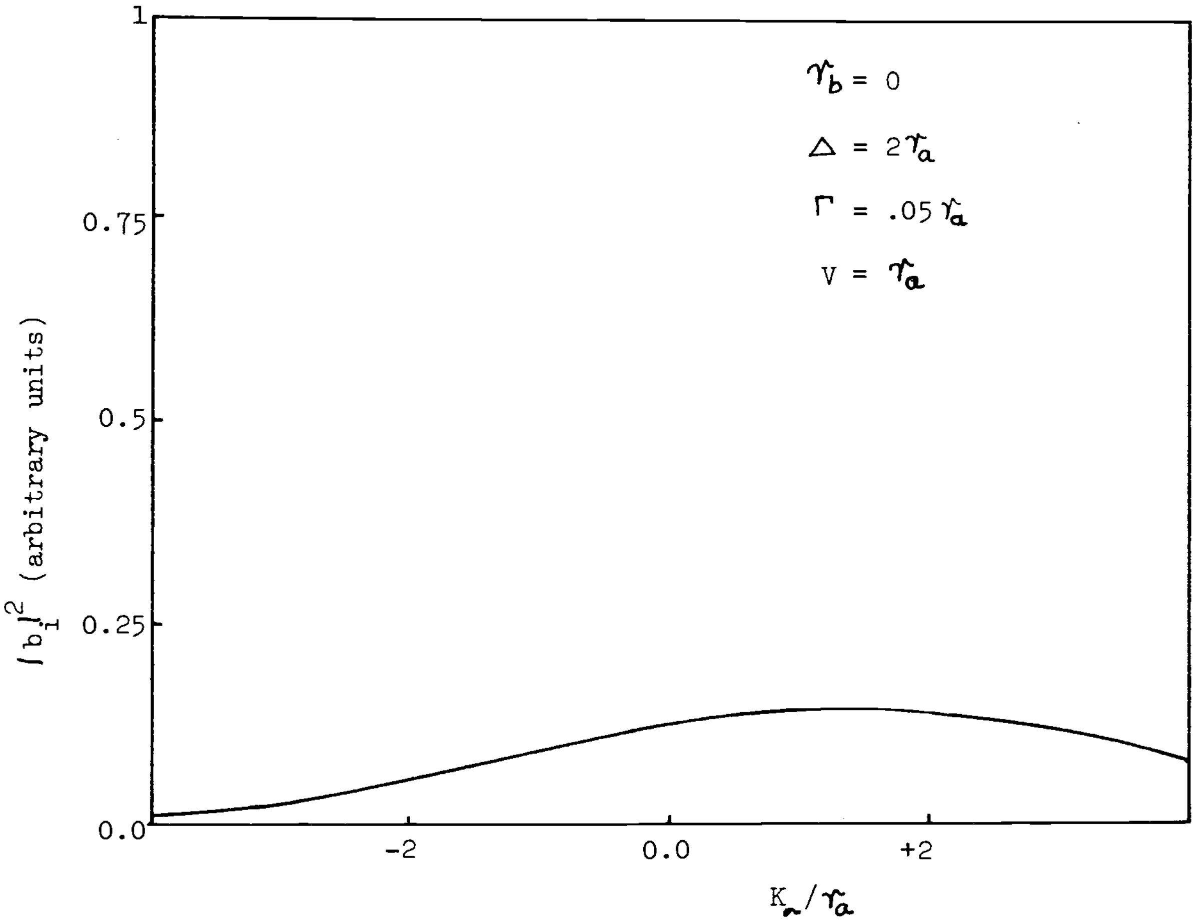

Fig. 3-4. The probability $|b_i|^2$ as a function of K_α $(K_\alpha = k_\alpha - (E'_a + E'_b)/2 + E'_c)$ at time $t = 1/\gamma_a$.

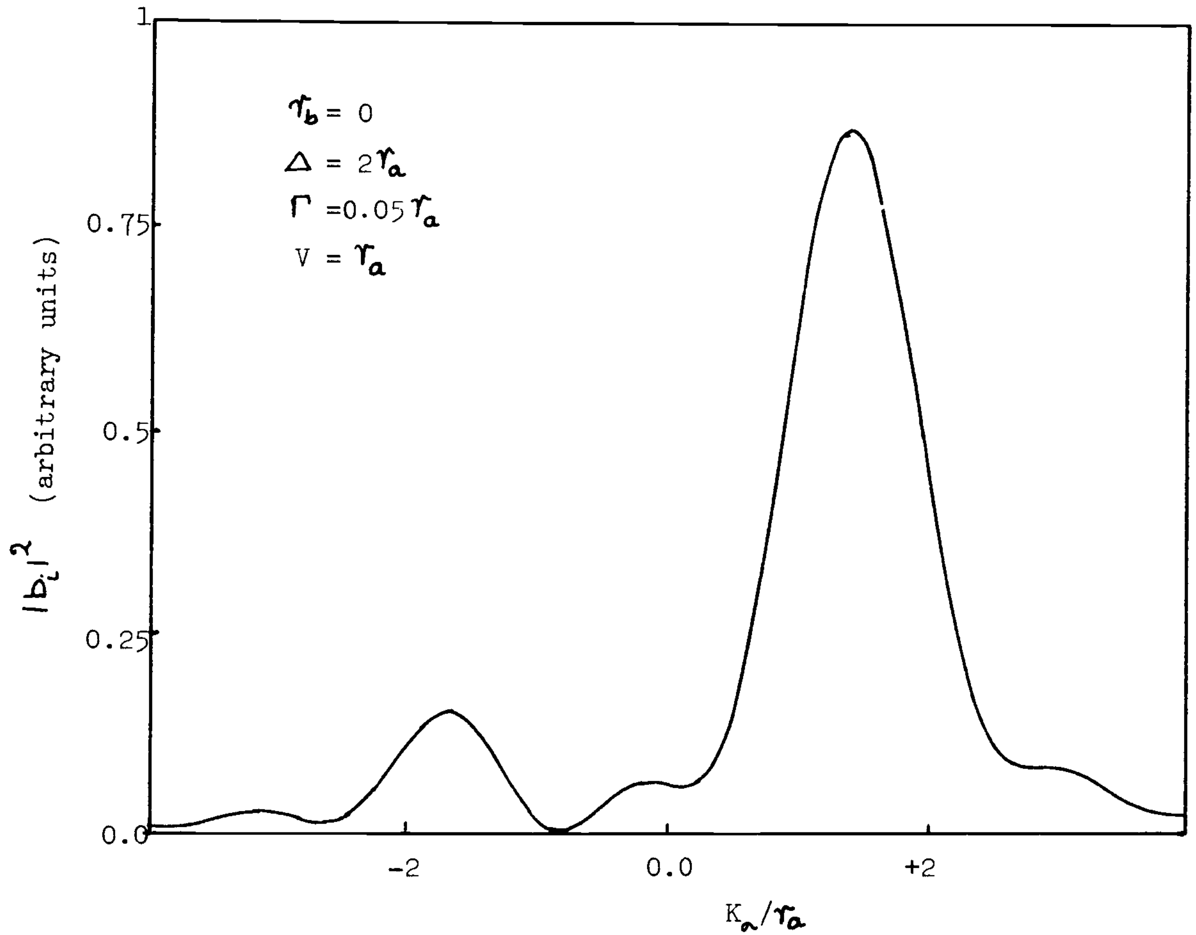

Fig. 3-5. The probability $|b_i|^2$ as a function of K_σ ($K_\sigma = k_\sigma - (E_a' + E_b')/2 + E_c'$) at time $t = 5/\gamma_a$

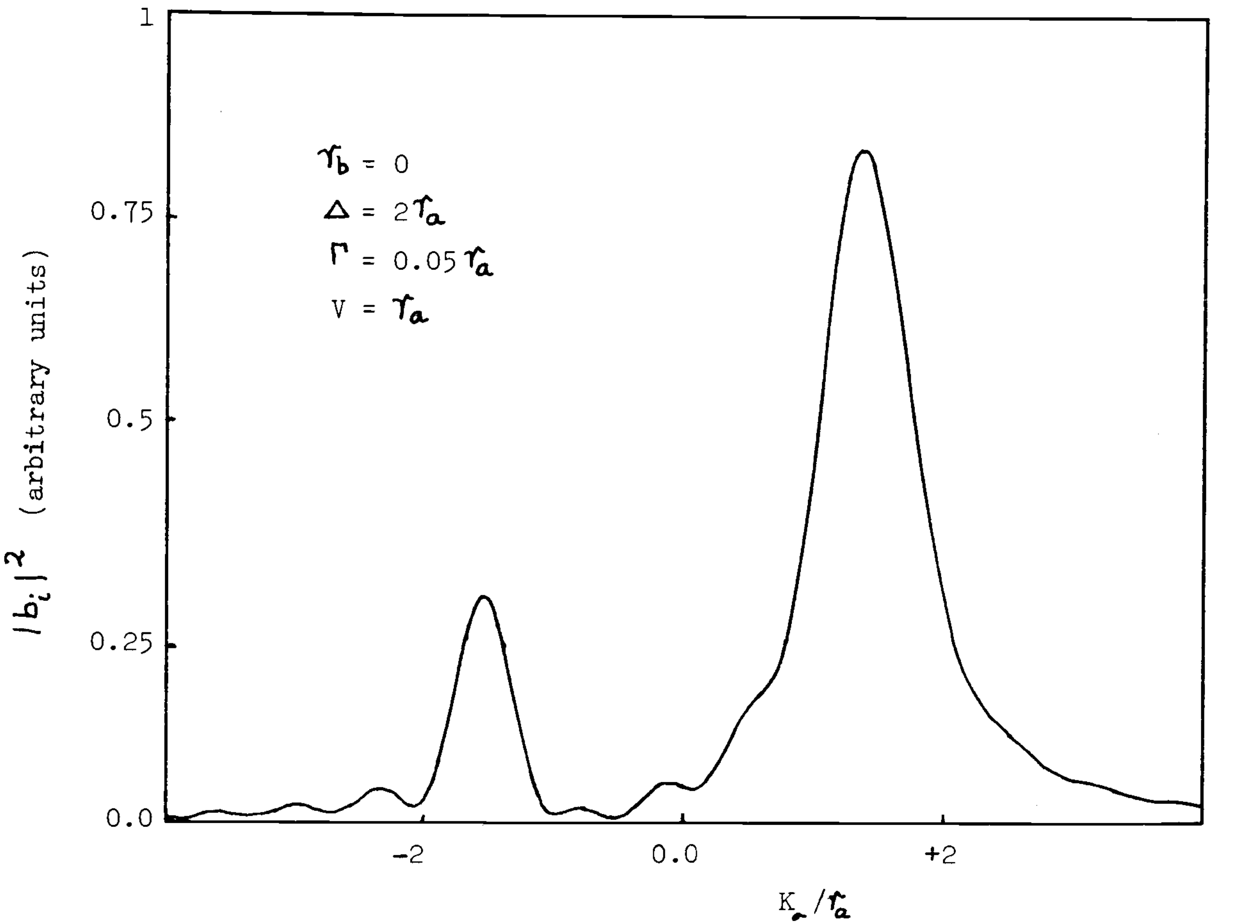

Fig. 3-6. The probability $|b_i|^2$ as a function of K_σ ($K_\sigma = k_\sigma - (E'_a + E'_b)/2 + E'_c$) at time $t = 10/\gamma_a$

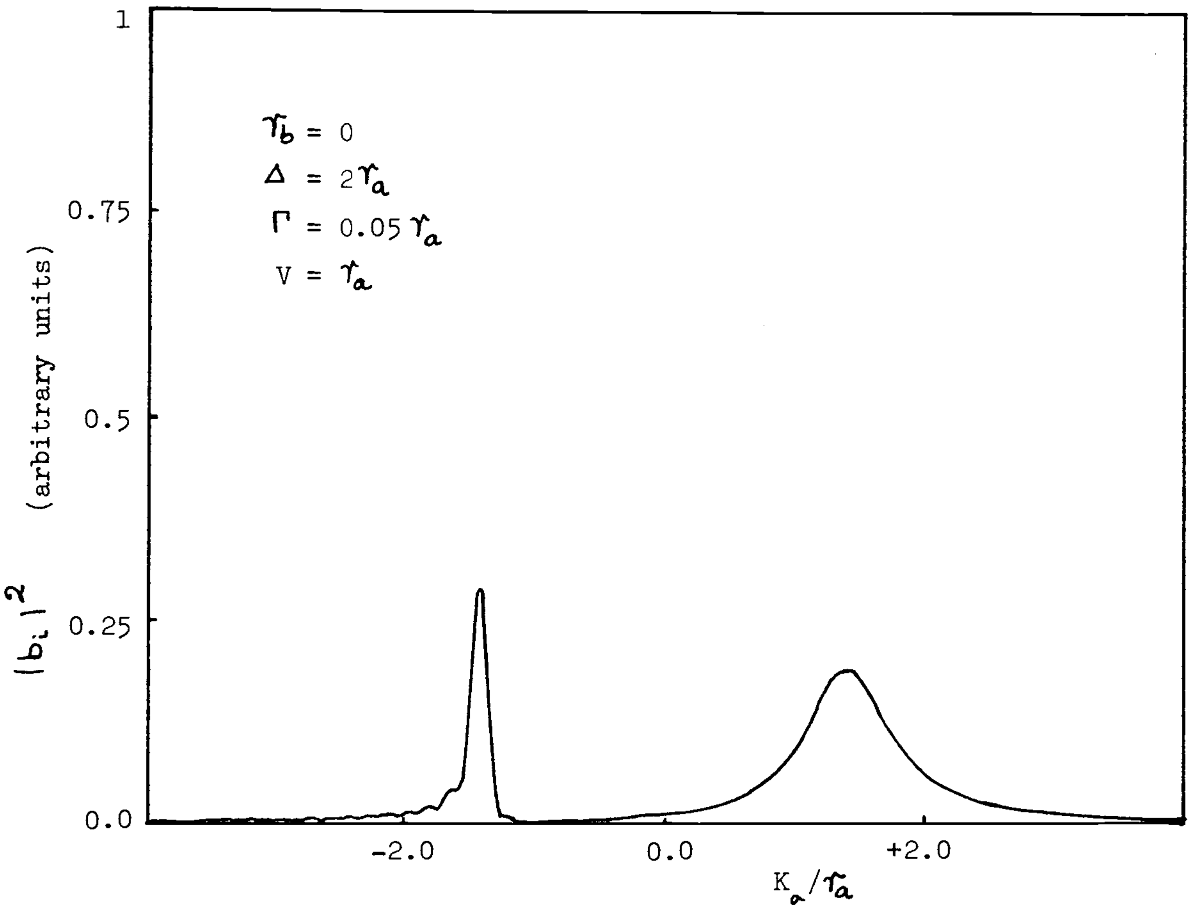

Fig. 3-7. The probability $|b_i(t)|^2$ as a function of K_σ ($K_\sigma = k_\sigma - (E_a' + E_b')/2 + E_c'$) at time $t = 40/\gamma_a$.

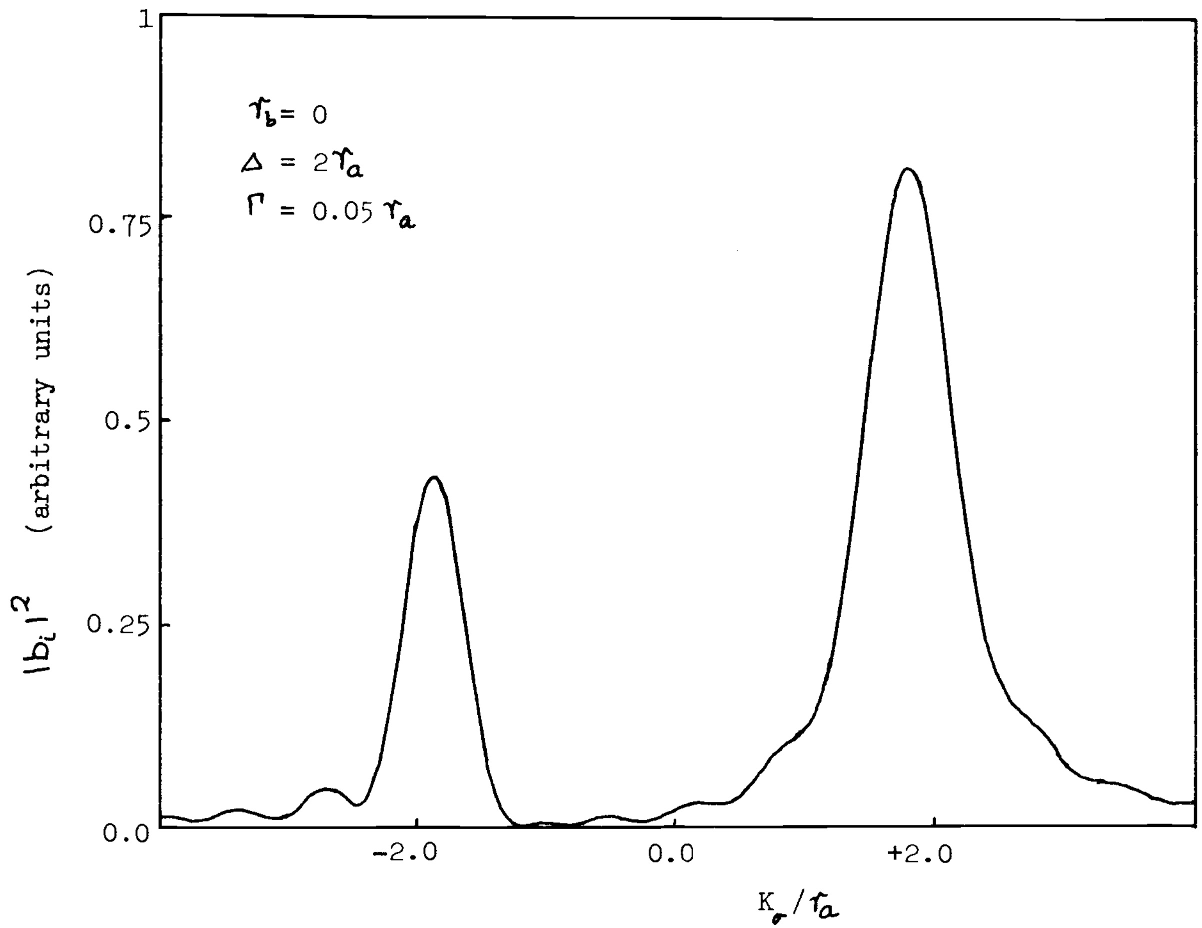

Fig. 3-8. The probability $|b_i|^2$ as a function of K_σ ($K_\sigma = k_\sigma - (E_a' + E_b')/2 + E_c'$) at time $t = 10/\gamma_a$ for $V = 1.5\,\gamma_a$.

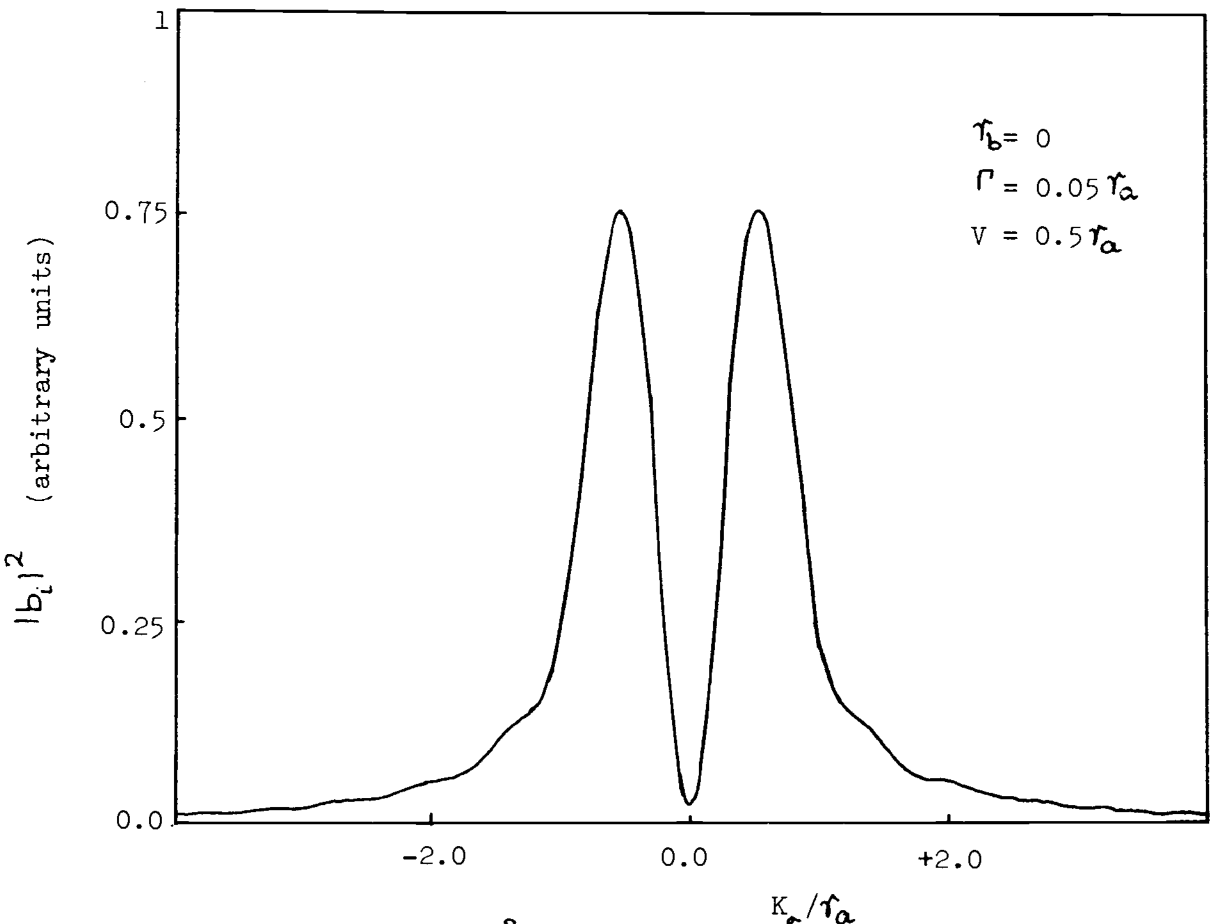

Fig. 3-9. The probability $|b_i(t)|^2$ as a function of K_α at time $t = 10/\gamma_a$ for $\Delta = 0$.

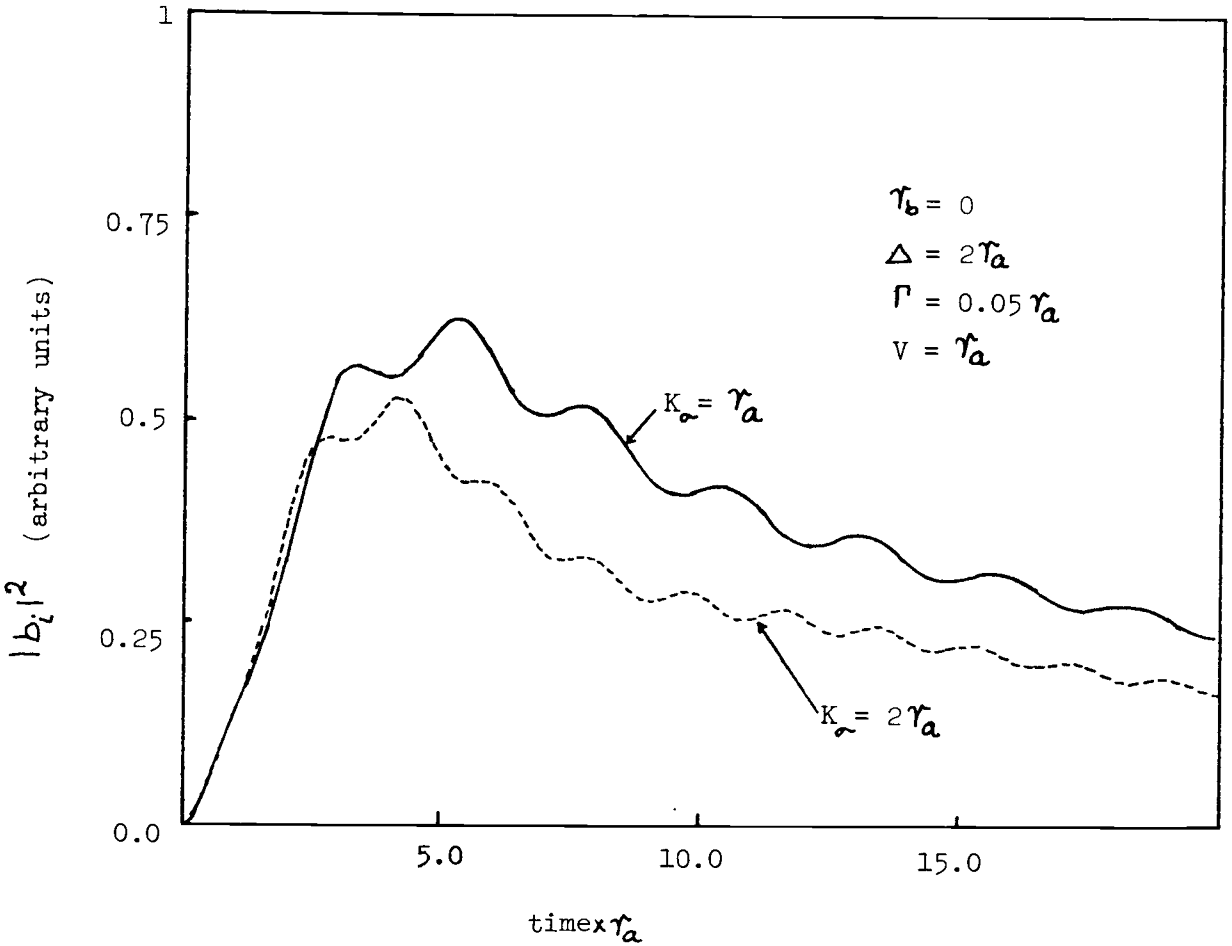

Fig. 3-10 The probability $|b_i|^2$ as a function of time t.

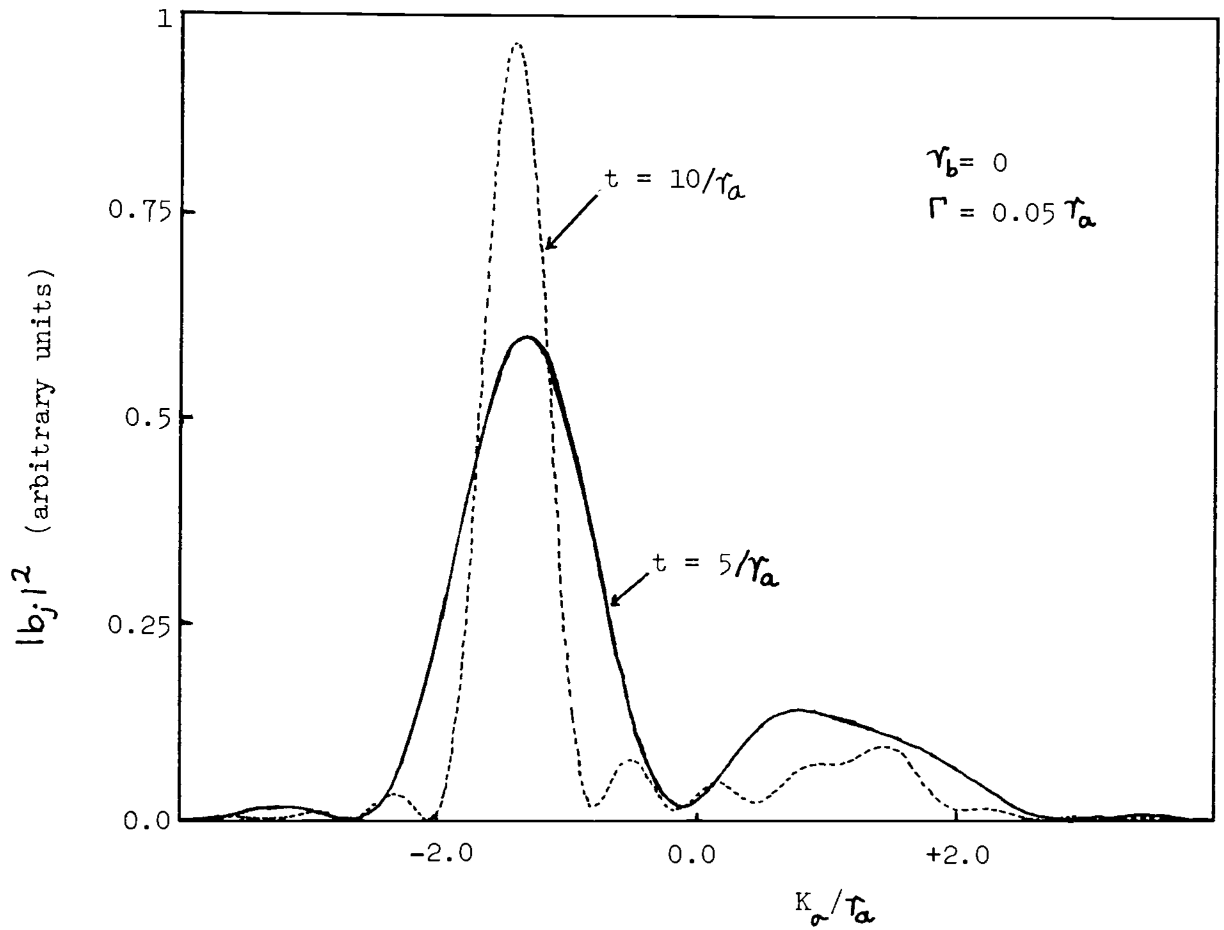

Fig. 3-11. The probability $|b_j|^2$ as a function of K_σ for $\Delta = 2\gamma_a$ and $V = \gamma_a$.

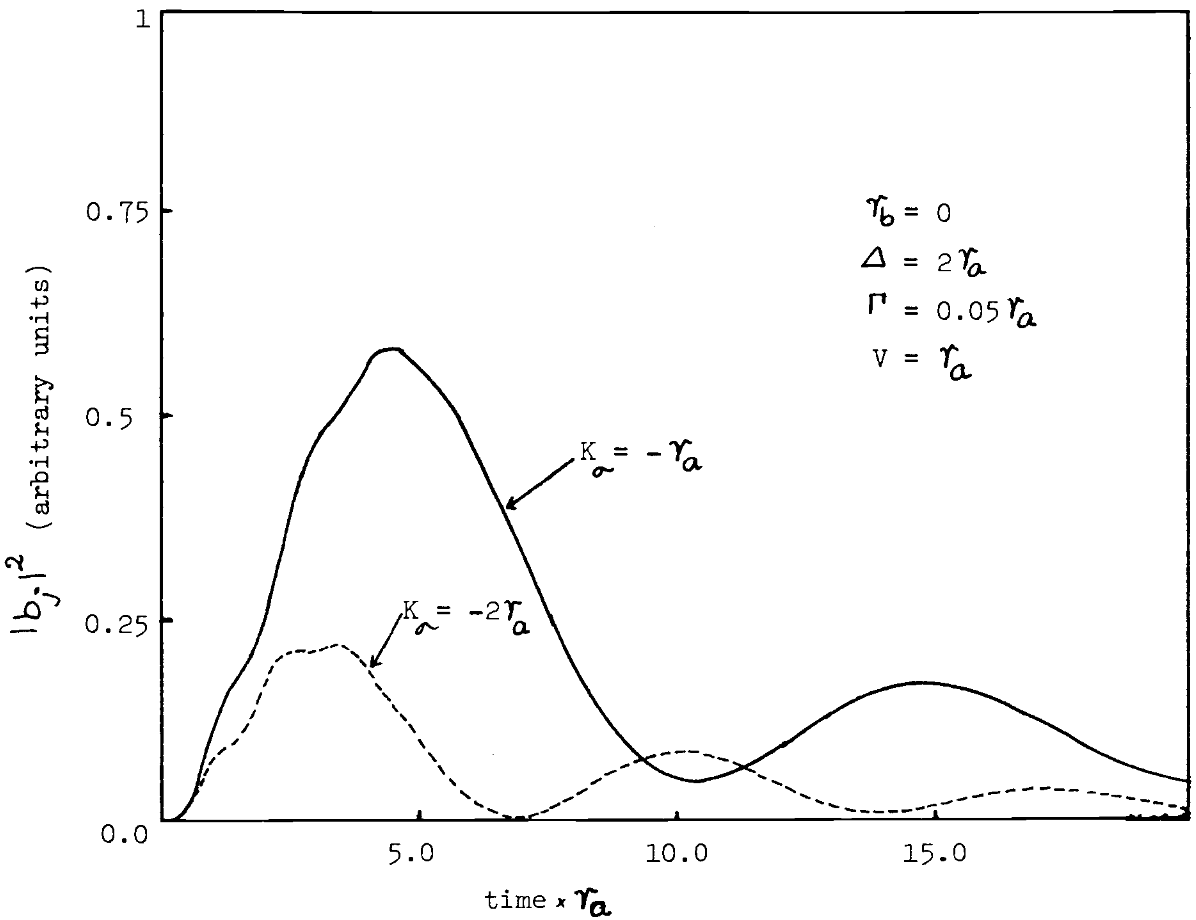

Fig. 3-12. The probability $|b_j|^2$ as a function of time t.

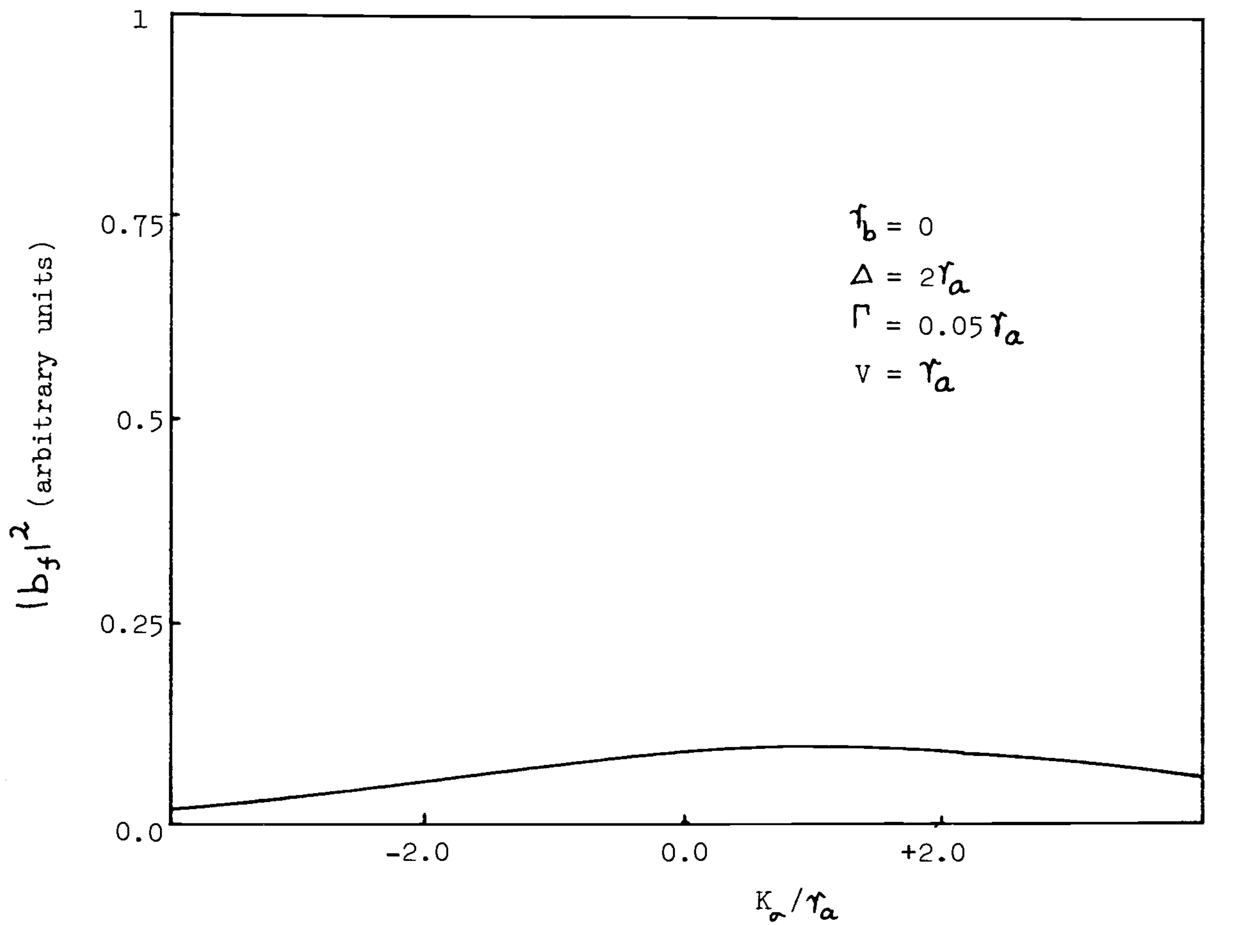

Fig. 3-13. The probability $|b_f|^2$ as a function of K_σ for $K_\lambda = \gamma_a$ at time $t = 1/\gamma_a$ ($K_\sigma = k_\sigma - (E_a' + E_b')/2 + E_c'$, $K_\lambda = k_\lambda - (E_a' + E_b')/2 + E_c'$).

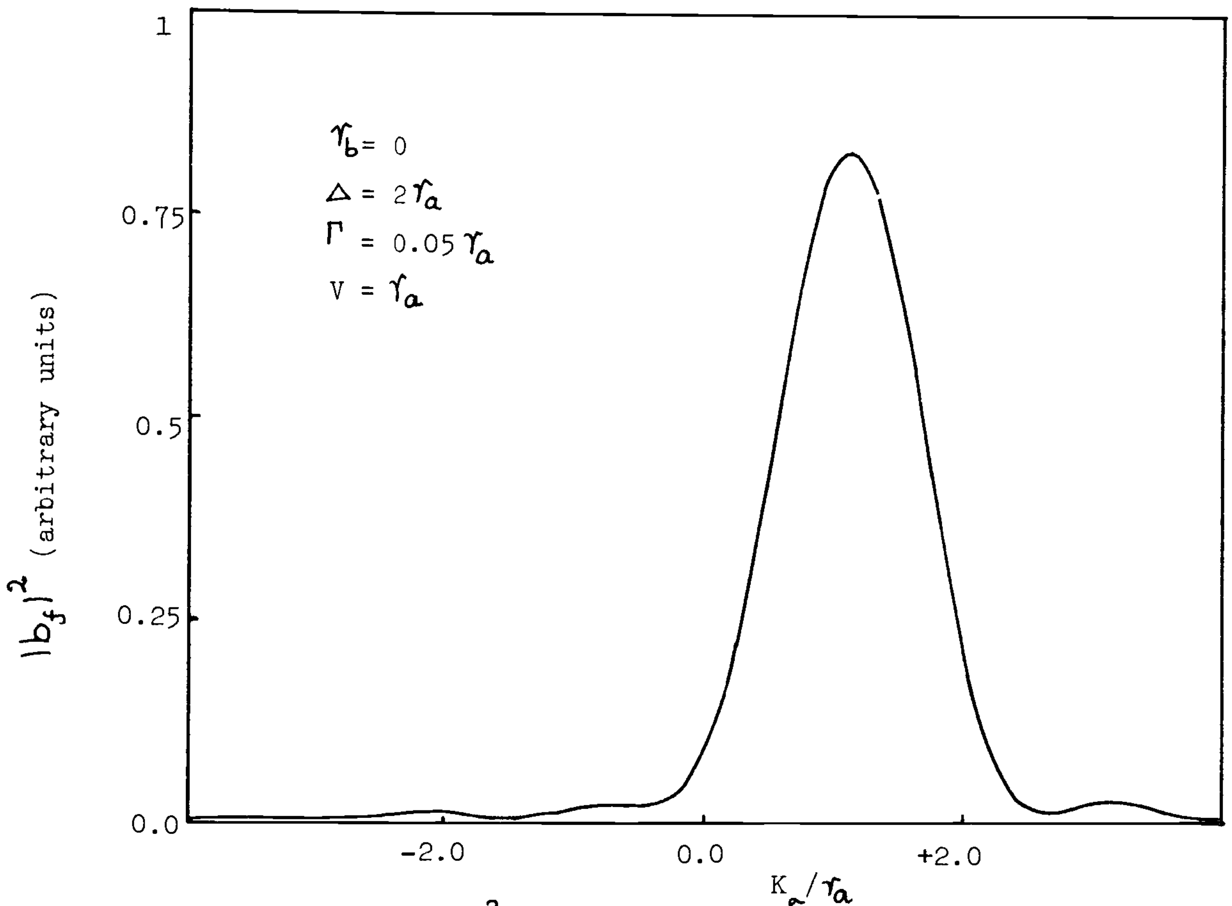

Fig. 3-14. The probability $|b_f|^2$ as a function of K_α for $K_\lambda = \gamma_a$ at time $t = 5/\gamma_a$. The ordinate is reduced by a factor of 1/20 compared to the ordinate in Fig. 3-13.

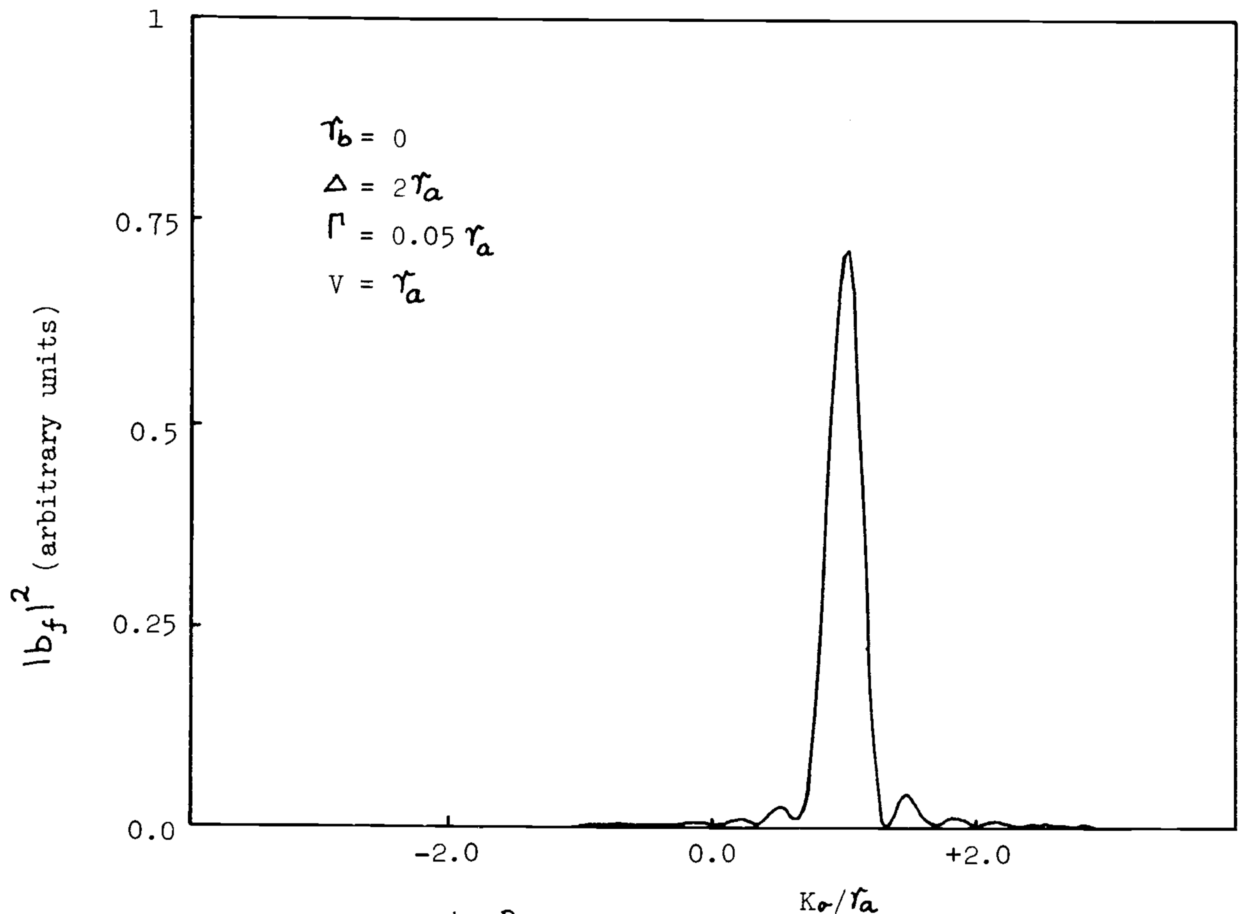

Fig. 3-15. The probability $|b_f|^2$ as a function of K_σ for $K_\lambda = \gamma_a$ at time $t = 20/\gamma_a$. The ordinate is reduced by a factor of 1/20 compared to the ordinate in Fig. 3-14.

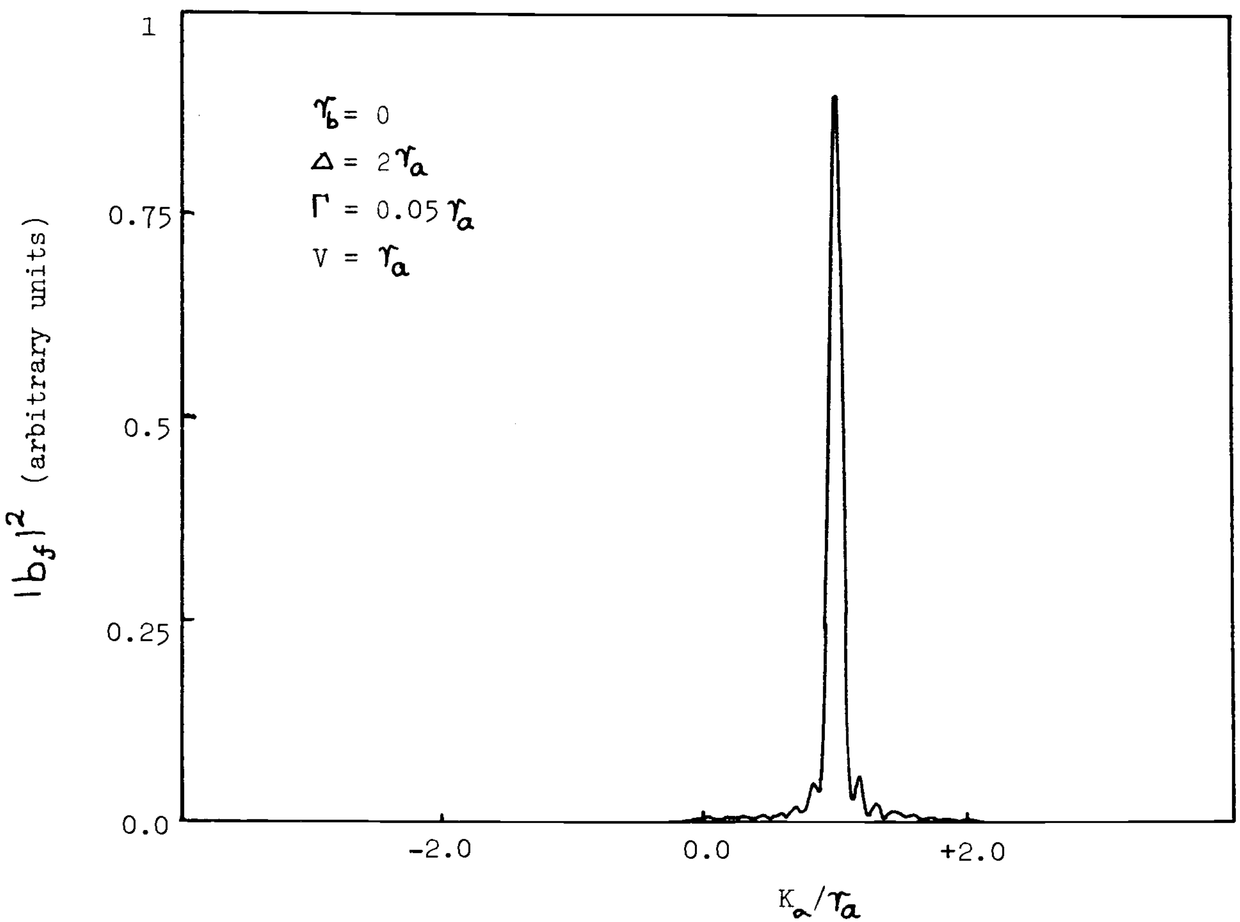

Fig. 3-16. The probability $|b_f|^2$ as a function of K_σ for $K_\lambda = \gamma_a$ at time $t = 50/\gamma_a$. The ordinate is reduced by a factor of 0.36 compared to the ordinate in Fig. 3-15.

C. Lineshape and Linewidth of Emitted Radiation

A study of the lineshape and linewidth of the emitted radiation for the case where $\Gamma_b = 0$ (state $|b\rangle$ is non-decaying) is presented in this section. An expression for $P(\hat{e}_\alpha, k_\lambda)$, the probability that a photon with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$ has been emitted between time $t = 0$ to $t \to \infty$, is obtained by setting P^λ_{cb} and P^α_{bc} in Eq.(2-60) equal to zero:

$$P(\hat{e}_\alpha, k_\lambda) = \frac{[e^4 I_0/(L^3 \Gamma k_0^3)]\,|P^\lambda_{ca}|^2 |P^\alpha_{ac}|^2 (K + \Delta/2)^2}{[(K-\Delta/2)(K+\Delta/2) - V^2]^2 + (K+\Delta/2)^2 \Gamma_a^2/4} \qquad (3\text{-}13)$$

This probability has two maxima, one at $K = \sqrt{\Delta^2 + 4V^2}/2$ and the other at $K = -(\Delta^2+4V^2)^{1/2}/2$. These maxima have equal hights but unequal linewidths. These linewidths are obtained as follows. The values of K for which $P(\hat{e}_\alpha, k_\lambda)$ is equal to half of it's maximum value, are determined from the equation:

$$\frac{(K+\Delta/2)^2}{[(K-\Delta/2)(K+\Delta/2) - V^2]^2 + (K+\Delta/2)^2 \Gamma_a^2/4} = \frac{2}{\Gamma_a^2}.$$

After simplifying the above equation, one gets:

$$(K^2 - \Delta^2/4 - V^2)^2 - (K - \Delta/2)^2\, \Gamma_a^2/4 = 0.$$

This equation gives four values of K for which $P(\hat{e}_\alpha, k_\lambda)$ is half its maximum value. The results are:

$$\left.\begin{matrix} K_1 \\ K_2 \end{matrix}\right\} = \Gamma_a/4 \pm \tfrac{1}{2}\left(\Gamma_a^2/4 + \Delta^2 + 4V^2 + \Gamma_a \Delta\right)^{\frac{1}{2}}$$

and

$$\left.\begin{matrix} K_3 \\ K_4 \end{matrix}\right\} = -\frac{\gamma_a}{4} \pm \frac{1}{2}\left(\gamma_a^2/4 + \Delta^2 + 4V^2 - \gamma_a\Delta\right)^{\frac{1}{2}}$$

The probability $P(\hat{e}_\mu, k_\lambda)$ is zero at $K = -\Delta/2$. Thus the width of the line at $K = \frac{1}{2}(\Delta^2+4V^2)^{\frac{1}{2}}$ is

$$\omega_1 = \gamma_a/2 + \frac{1}{2}\Big[\left(\gamma_a^2/4 + \Delta^2 + 4V^2 + \gamma_a\Delta\right)^{\frac{1}{2}} - \left(\gamma_a^2/4 + \Delta^2 + 4V^2 - \gamma_a\Delta\right)^{\frac{1}{2}}\Big] \qquad (3\text{-}14)$$

and the width of the line at $K = -\frac{1}{2}(\Delta^2+4V^2)^{\frac{1}{2}}$ is

$$\omega_2 = \gamma_a/2 - \frac{1}{2}\Big[\left(\gamma_a^2/4 + \Delta^2 + 4V^2 + \gamma_a\Delta\right)^{\frac{1}{2}} - \left(\gamma_a^2/4 + \Delta^2 + 4V^2 - \gamma_a\Delta\right)^{\frac{1}{2}}\Big] \qquad (3\text{-}15)$$

The two linewidths add up to γ_a (the linewidth of the single line when no coupling is considered). As V increases, the linewidth ω_1, decreases and ω_2 increases. But as Δ increases, ω_1 increases and ω_2 decreases. Both linewidths approach $\gamma_a/2$ when $V \to \infty$. For $\Delta = 0$, the two linewidths reduce to the same value $\gamma_a/2$, and thus are independent of V.

For $\Delta = .5\gamma_a$, the probability $P(\hat{e}_\mu, k_\lambda)$ is plotted in Figs. 3-17 to 3-19 as a function of K for different V. Figure 3-17 shows that only one emission line of linewidth γ_a is observed when V = 0. In

Fig.3-18 where $V = .2\gamma_a$, a "hole" is observed in the emission line at $K = - .25\gamma_a$ ($k_\lambda = E_b' - E_c'$). This "hole" becomes wider with increasing coupling strength V. The change in V and Δ also effects the linewidths as discussed earlier (compare Fig. 3-18 and Fig. 3-19 for the effect of V and Fig. 3-19 and Fig. 3-20 for the effect of Δ).

For $\Delta = 0$, the probability $P(\hat{e}_\sim, k_\lambda)$ is plotted in Figs. 3-21 to 3-23 as a function of K for different values of V. Comparing Fig. 3-21 and Fig. 3-22, one finds that one Lorentzian line centered at K = 0 for V = 0 splits up into two lines for $V = .2\gamma_a$ with a "hole" at K = 0. Figure 3-22 and Fig. 3-23 show that as V increases the two lines move farther away from K = 0 without changing their linewidths. Thus the linewidth in this case is independent of V and is equal to $\gamma_a/2$ (half of the linewidth of the line when V = 0).

A physical explaination of the linewidth and lineshape of the emitted radiation can be presented in the following way. The external coupling V mixes the two excited states unequally for $\Delta \neq 0$. Thus state $|a\rangle$ has some probability at energy E_1(perturbed energy corresponding to state $|a\rangle$) and a lower probability at E_2(perturbed energy corresponding to state $|b\rangle$). As V increases, the probability of the atom in the state $|a\rangle$ at the energy E_2 increases and the probability at E_1 decreases. This increase in probability at E_2 and decrease in probability at E_1 explains the increase in the linewidth of the line at E_2 and decrease in the linewidth of the line at E_1. For $\Delta = 0$, the two states are mixed equally, thus the probability of the decaying state $|a\rangle$ at the energies E_1 and E_2 are equal for any value of V.

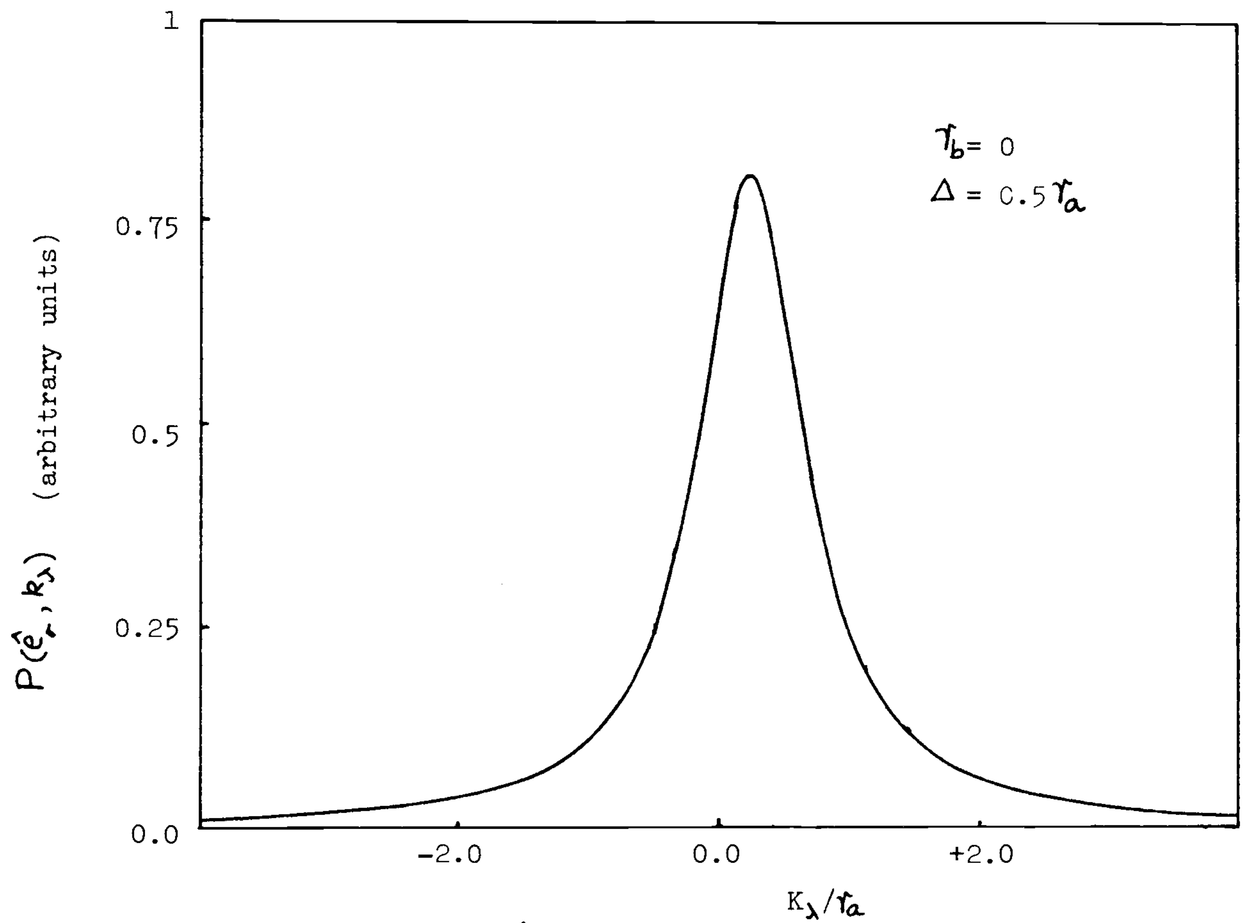

Fig. 3-17. The probability $P(\hat{e}_r, k_\lambda)$ as a function of K_λ ($K_\lambda = k_\lambda - (E'_a + E'_b)/2 + E'_c$) for $V = 0$. The maximum is at $K_\lambda = 0.25\gamma_a$.

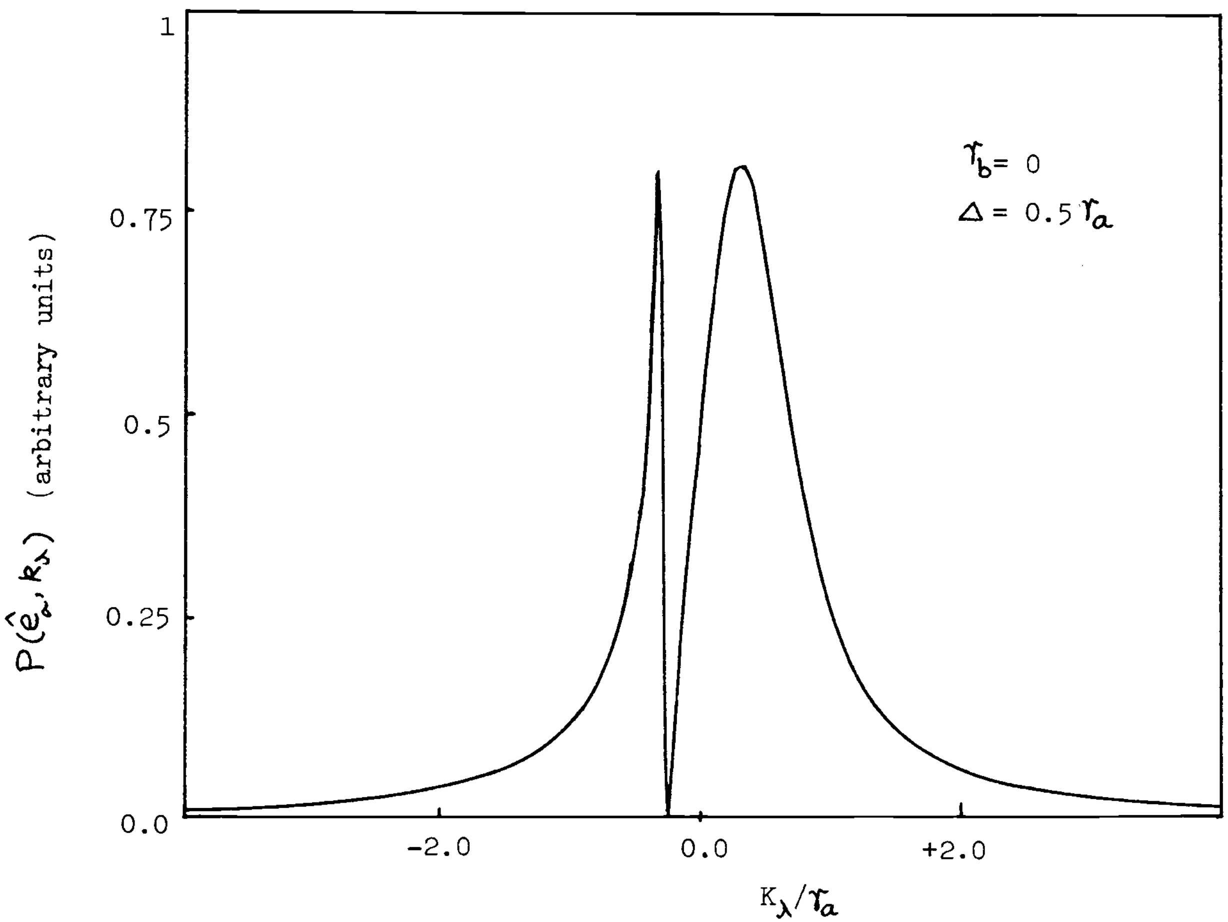

Fig. 3-18. The probability $P(\hat{e}_\alpha, k_\lambda)$ as a function of K_λ for $V = 0.2\gamma_a$.
A "hole" appears at $K_\lambda = -0.25\gamma_a$.

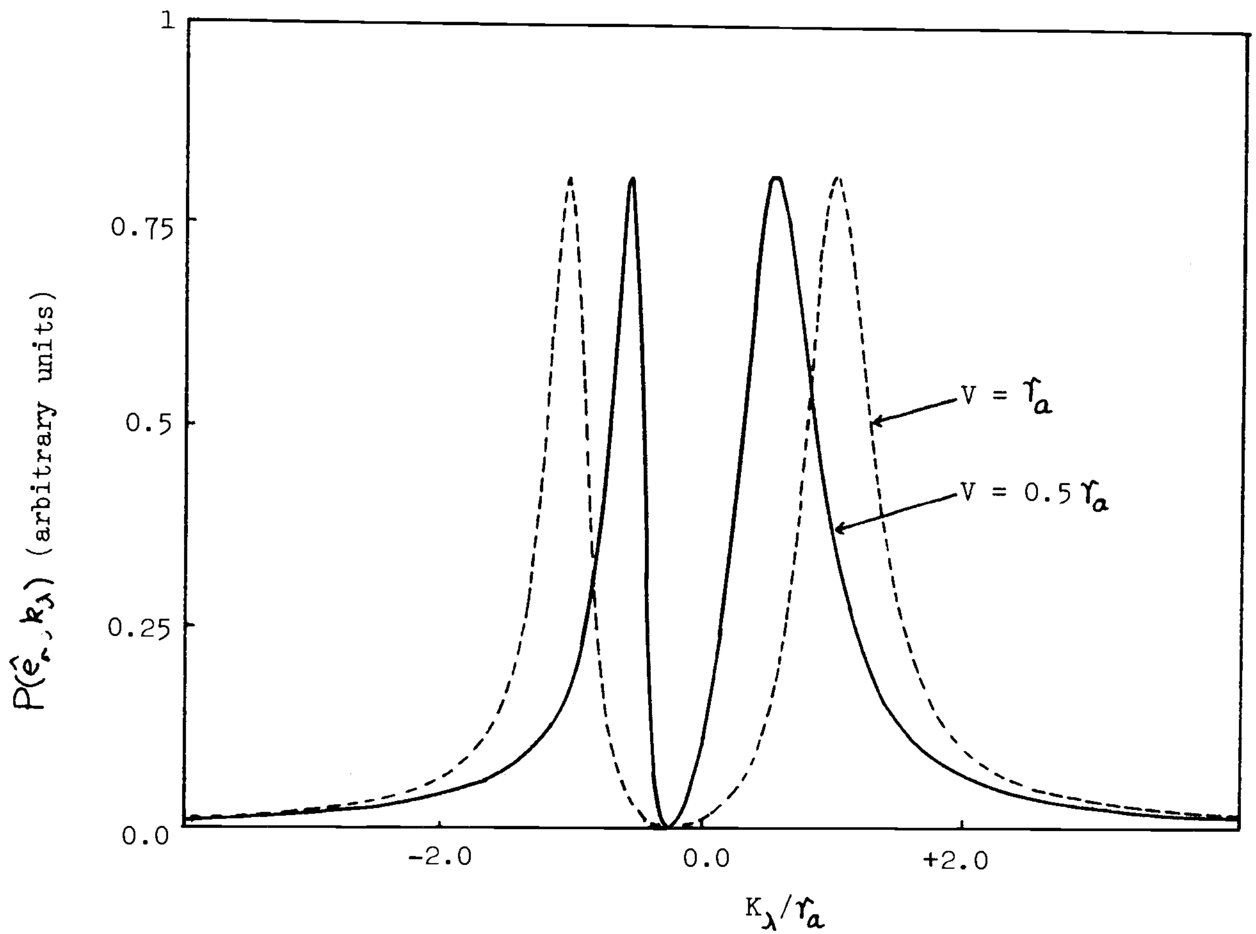

Fig. 3-19. The probability $P(\hat{e}_\alpha, k_\lambda)$ as a function of K_λ for $\Delta = 0.5\gamma_a$ and $\gamma_b = 0$.

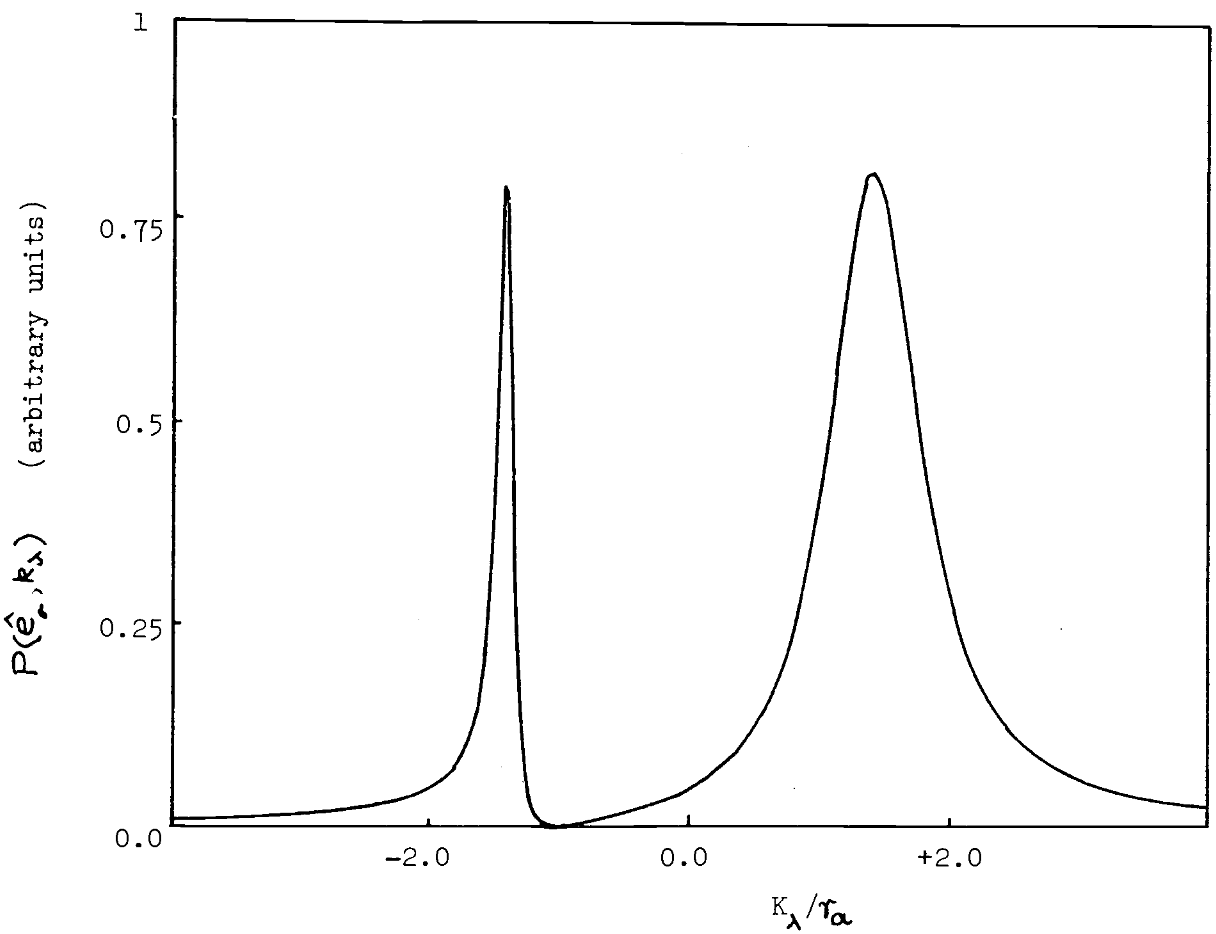

Fig. 3-20. The probability $P(\hat{e}_\sigma, k_\lambda)$ as a function of K_λ for $\Delta = 2\gamma_a$, $V = \gamma_a$ and $\gamma_b = 0$.

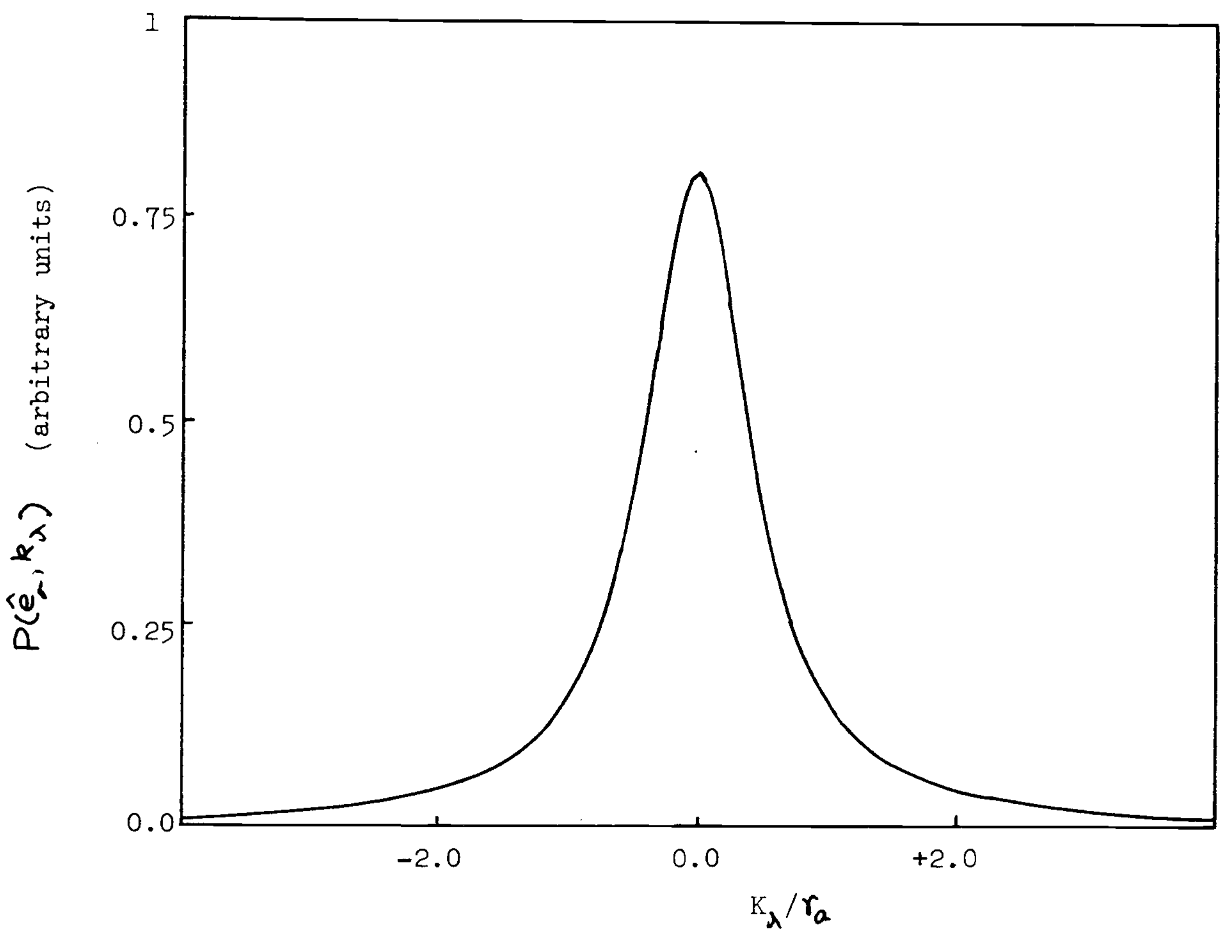

Fig. 3-21. The probability $P(\hat{e}_r, k_\lambda)$ as a function of K_λ for $\Delta = 0$, $V = 0$ and $\gamma_b = 0$.

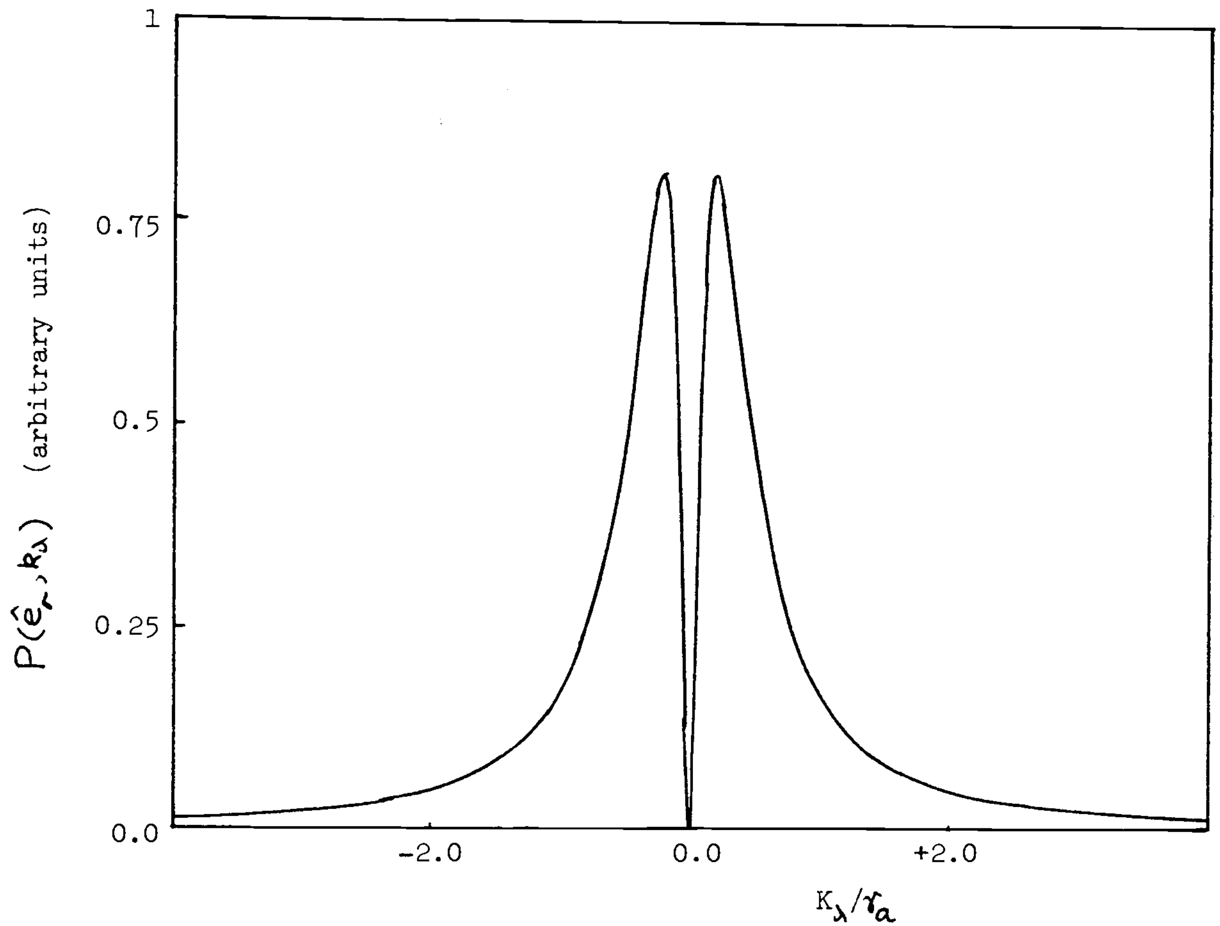

Fig. 3-22. The probability $P(\hat{e}_r, k_\lambda)$ as a function of K_λ for $\Delta = 0$, $V = 0.2\gamma_a$ and $\gamma_b = 0$.

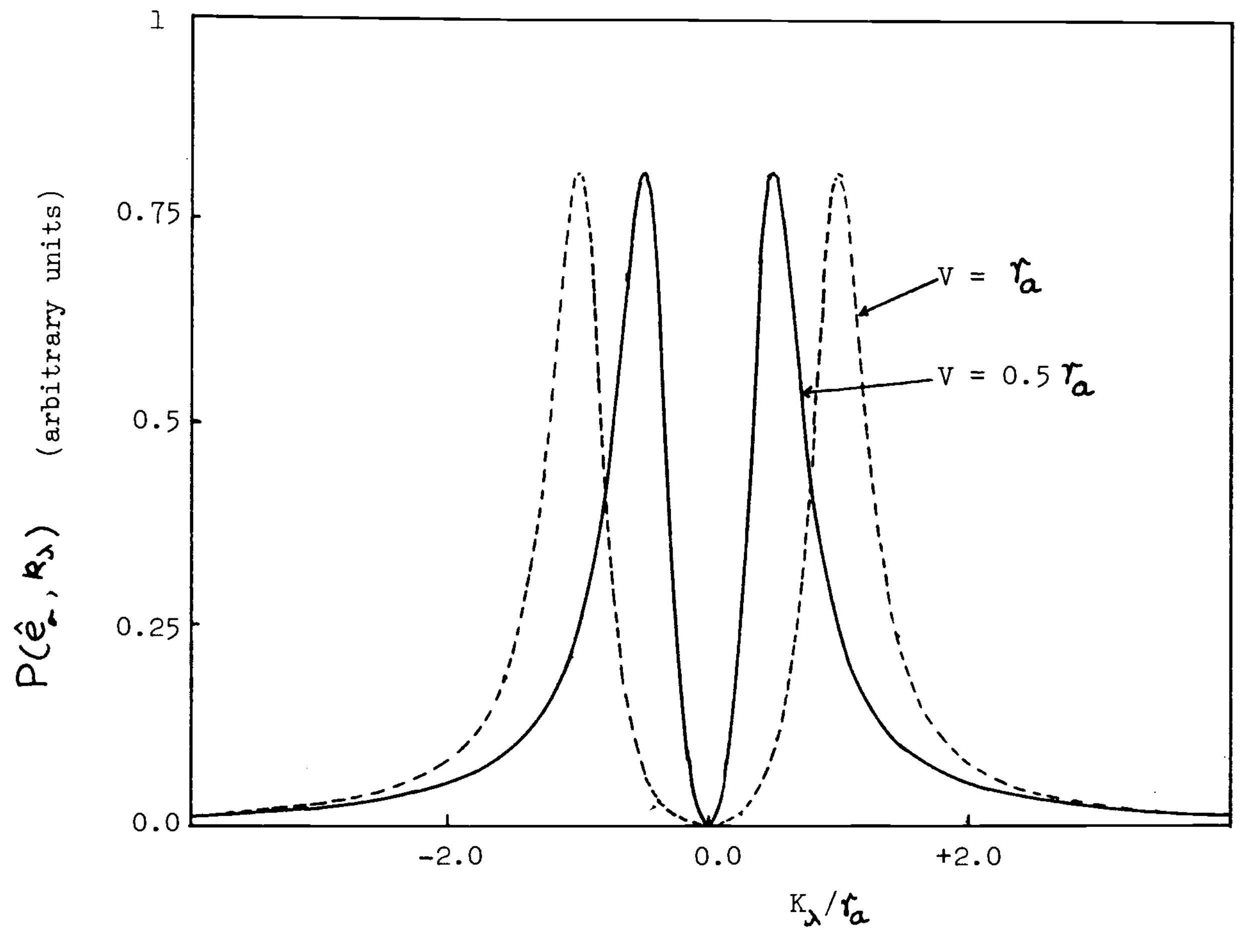

Fig. 3-23. The probability $P(\hat{e}_r, k_\lambda)$ as a function of K_λ for $\Delta = 0$ and $\gamma_b = 0$.

Therefore the linewidths are independent of V.

The "hole" in the emission line can be attributed to an interference phenomenon. If one solves for the eigenstates of the Hamiltonian of the atom plus the external perturbation, in terms of the states $|a\rangle$ and $|b\rangle$, then one gets two eigenstates which are not coupled any more by the external static field. If the radiation field is now allowed to interact with the atom then the two eigenstates decay by emitting photons. The amplitudes of these eigenstates at the energy E_b' are such that the photons emitted at that frequency interfere distructively and produce a "hole" in the emission line. A similar "hole" was observed by Lamb and Retherford (17) in atomic Hydrogen for $2^2S_{1/2\ 1/2}$, $2^2S_{1/2 -1/2}$ and $2^2P_{1/2\ 1/2}$ states. An external rf field couples the states.

IV. RESONANCE FLUORESCENCE WITH TWO DECAYING EXCITED STATES WITH EQUAL DECAY CONSTANTS

The theory developed in Chapter II is used here to discuss the resonance scattering of radiation from an atomic system where both the excited states decay with equal decay constants ($\gamma_a = \gamma_b$).

The probabilities $|b_i|^2$, $|b_j|^2$ and $|b_f|^2$ as a function of time t have similar features as those of the probabilities discussed in Chapter III and thus they are not discussed here.

A study of linewidth and lineshape of the scattered radiation is presented in the next section. In section B of this chapter an expression for the total intensity of the scattered radiation is derived for a given direction and polarization of the incident and the scattered beam. In section C, this intensity is calculated for the 2^2P state in Li^7 as a function of an external magnetic field.

A. Lineshape and Linewidth of Emitted Radiation

The expression for the probability $P(\hat{e}_\sigma, k_\lambda)$ that a photon has been emitted between time t = 0 and t = ∞ with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$ is obtained from Eq.(2-60) by setting $\gamma_a = \gamma_b = \gamma$:

$$P(\hat{e}_\sigma, k_\lambda) = \frac{e^4 I_0}{L^3 \Gamma k_0^3} \cdot \Big[\{ (K+\Delta/2)^2 + \gamma^2/4 \} |P_{ca}^{\lambda}|^2 |P_{ac}^{\sigma}|^2$$

$$+ \{ (K-\Delta/2)^2 + \gamma^2/4 \} |P_{cb}^{\lambda}|^2 |P_{bc}^{\sigma}|^2 + V^2 \{ |P_{ca}^{\lambda}|^2 |P_{bc}^{\sigma}|^2$$

$$+ |P_{cb}^{\lambda}|^2 |P_{ac}^{\sigma}|^2 + 4\,\mathrm{Re}(P_{ca}^{\lambda} P_{cb}^{\lambda *})\,\mathrm{Re}(P_{ac}^{\sigma} P_{bc}^{\sigma *}) - 2\,\mathrm{Re}(P_{ca}^{\lambda} P_{cb}^{\lambda *} P_{ac}^{\sigma} P_{bc}^{\sigma *})$$

$$+ 2V[\{(K+\Delta/2)|p_{ca}^{\lambda}|^2 + (K-\Delta/2)|p_{cb}^{\lambda}|^2\} \mathrm{Re}(p_{ac}^{\sigma} p_{bc}^{\sigma *})$$

$$+ \{(K+\Delta/2)|p_{ac}^{\sigma}|^2 + (K-\Delta/2)|p_{bc}^{\sigma}|^2\} \mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *})$$

$$+ \gamma/2 \{(|p_{cb}^{\lambda}|^2 - |p_{ca}^{\lambda}|^2) \mathrm{Im}(p_{ac}^{\sigma} p_{bc}^{\sigma *}) + (|p_{bc}^{\sigma}|^2 - |p_{ac}^{\sigma}|^2) \mathrm{Im}(p_{ca}^{\lambda} p_{cb}^{\lambda *})\}$$

$$+ (K^2 - \Delta^2/4 + \gamma^2/4)\, 2. \mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *})$$

$$+ \gamma\Delta/2\, \mathrm{Im}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *})] \times$$

$$[\{(K-R)^2 + \gamma^2/4\}\{(K+R)^2 + \gamma^2/4\}]^{-1} , \qquad (4\text{-}1)$$

where

$$K = k_{\lambda} - (E_a' + E_b')/2 + E_c' ,$$

$$R = \tfrac{1}{2}(\Delta^2 + 4V^2)^{\frac{1}{2}} ,$$

and

$$\Delta = E_a' - E_b' .$$

The matrix elements p_{ij}^{ℓ} for i,j = a, b and $\ell = \lambda, \sigma$ are defined in Eq.(A-4).

From Eq.(4-1), one finds that this probability has two maxima, one near K = R and other near K = - R. The probability $P(\hat{e}_{\sigma}, k_{\lambda})$ is plotted as a function of K in Figure 4-1 for different V_{ab} . For these graphs, the matrix elements are chosen such that $p_{ca}^{\lambda} = p_{cb}^{\lambda}$ and $p_{ac}^{\sigma} = p_{bc}^{\sigma}$ and are real.

Figure 4-1 shows that the increase in V suppresses the maximum near K = - R and enhances the maximum near K = R. This effect is easily understood if one thinks in terms of the eigenstates of the perturbed Hamiltonian (H_o + V) {see Appendix C} . The two

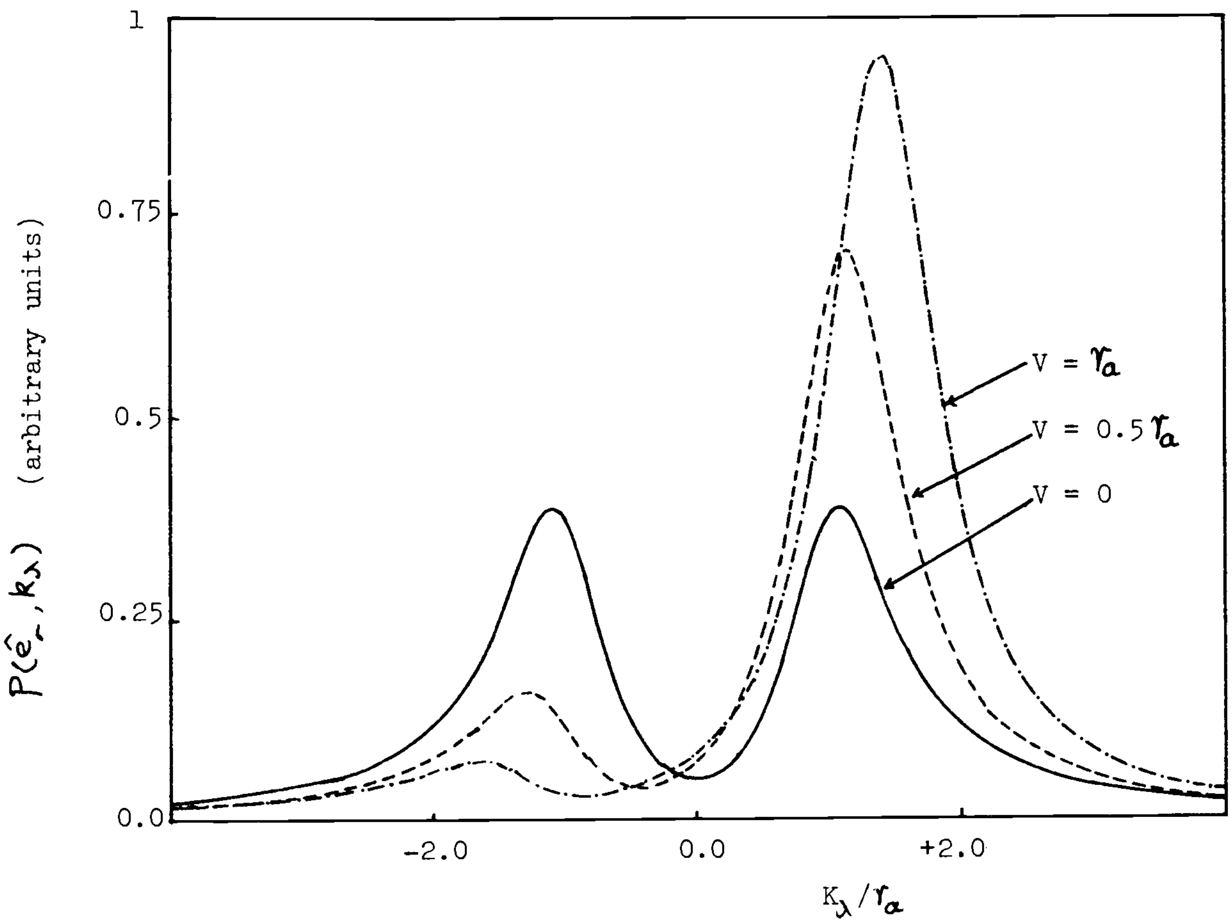

Fig. 4-1. The probability $P(\hat{e}_-, k_\lambda)$ as a function of K_λ for $\Delta = 2\gamma_a$ and $\gamma_a = \gamma_b \neq 0$.

eigenstates of this Hamiltonian are $C_o|a\rangle + D_o|b\rangle$ and $-D_o|a\rangle + C_o|b\rangle$ and have energies equal to $(E_a' + E_b')/2 + R$ and $(E_a' + E_b')/2 - R$, respectively. The coefficients C_o and D_o are defined in Eq.(C-10). As V increases C_o decreases and D_o increases. Thus due to the sign difference in the eigenstates, the probability of photon emission from the state $C_o|a\rangle + D_o|b\rangle$ is greater than the probability from the state $-D_o|a\rangle + C_o|b\rangle$.

B. Intensity of Scattered Radiation

The intensity of the scattered radiation for a given direction and polarization of the incident and the scattered beams is obtained by setting $X_a = X_b = \pi/2$ in Eq.(2-62):

$$
\begin{aligned}
I(\Omega_a, \Omega_e, \sigma, \lambda) = \frac{e^4 I_o(1/\gamma)}{4\pi^2 \Gamma k_o} \Big[& |p_{ca}^\lambda|^2 |p_{ac}^\sigma|^2 + |p_{cb}^\lambda|^2 |p_{bc}^\sigma|^2 \\
& + \big[2V^2 \{ 4 Re(p_{ca}^\lambda p_{cb}^{\lambda *}) Re(p_{ac}^\sigma p_{bc}^{\sigma *}) - (|p_{ca}^\lambda|^2 - |p_{cb}^\lambda|^2)(|p_{ac}^\sigma|^2 - |p_{bc}^\sigma|^2) \} \\
& + 2V \{ \Delta \{ (|p_{ca}^\lambda|^2 - |p_{cb}^\lambda|^2) Re(p_{ac}^\sigma p_{bc}^{\sigma *}) + (|p_{ac}^\sigma|^2 - |p_{bc}^\sigma|^2) Re(p_{ca}^\lambda p_{cb}^{\lambda *}) \} \\
& - \gamma \{ (|p_{ca}^\lambda|^2 - |p_{cb}^\lambda|^2) Im(p_{ac}^\sigma p_{bc}^{\sigma *}) \\
& + (|p_{ac}^\sigma|^2 - |p_{bc}^\sigma|^2) Im(p_{ca}^\lambda p_{cb}^{\lambda *}) \} \} \\
& + 2\gamma^2 Re(p_{ca}^\lambda p_{cb}^{\lambda *} p_{ac}^\sigma p_{bc}^{\sigma *}) + 2\Delta\gamma Im(p_{ca}^\lambda p_{cb}^{\lambda *} p_{ac}^\sigma p_{bc}^{\sigma *}) \big] \times \\
& (\Delta^2 + 4V^2 + \gamma^2)^{-1} \Big]
\end{aligned}
\tag{4-2}
$$

As discussed earlier in Chapter II section D, the first two terms in Eq.(4-2) are constant. These terms arise from the direct resonance fluorescence process. The next six terms arise from the presence of the non-diagonal matrix elemement V_{ab}. These terms are called anti-crossing signals. The last two terms are crossing signals. The name anti-crossing and crossing are used because the energy levels repel and cross each other, respectively, when plotted as a function of the external perturbation.

The crossing signal is pure Lorentzian or dispersion as a function of the energy difference Δ depending on whether $P^{\lambda}_{ca}P^{\lambda *}_{cb}P^{\sigma}_{ac}P^{\sigma *}_{bc}$ is real or imaginary, respectively. If it is a pure Lorentzian then it has a half width equal to $(4V^2+\gamma^2)^{\frac{1}{2}}$.

Separating the crossing and anti-crossing signals from Eq.(4-2), one gets:

$$S_C \propto \frac{2\gamma\, Re(P^{\lambda}_{ca}P^{\lambda *}_{cb}P^{\sigma}_{ac}P^{\sigma *}_{bc}) + 2\Delta\, Im(P^{\lambda}_{ca}P^{\lambda *}_{cb}P^{\sigma}_{ac}P^{\sigma *}_{bc})}{\Delta^2 + 4V^2 + \gamma^2} \tag{4-3}$$

and

$$\begin{aligned} S_A \propto \Big[& 2V^2\{4Re(P^{\lambda}_{ca}P^{\lambda *}_{cb})Re(P^{\sigma}_{ac}P^{\sigma *}_{bc}) - (|P^{\lambda}_{ca}|^2 - |P^{\lambda}_{cb}|^2)\times \\ & (|P^{\sigma}_{ac}|^2 - |P^{\sigma}_{bc}|^2)\} + 2V\{\Delta\{(|P^{\sigma}_{ac}|^2 - |P^{\sigma}_{bc}|^2)Re(P^{\lambda}_{ca}P^{\lambda *}_{cb}) \\ & + (|P^{\lambda}_{ca}|^2 - |P^{\lambda}_{cb}|^2)Re(P^{\sigma}_{ac}P^{\sigma *}_{bc})\} - \gamma\{(|P^{\lambda}_{ca}|^2 - |P^{\lambda}_{cb}|^2)Im(P^{\sigma}_{ac}P^{\sigma *}_{bc}) \\ & + (|P^{\sigma}_{ac}|^2 - |P^{\sigma}_{bc}|^2)Im(P^{\lambda}_{ca}P^{\lambda *}_{cb})\}\}\times \\ & (\Delta^2 + 4V^2 + \gamma^2)^{-1}\Big] \end{aligned} \tag{4-4}$$

where S_C and S_A stand for the crossing and anti-crossing signals, respectively. The above signals depend on the direction and polarization of the incident and the scattered radiation.

For an atom which has many coupled excited states with equal decay constants Γ (coupled by an external static perturbation) and many ground states, the intensity of the scattered beam is calculated in the following way.

The total Hamiltonian of the atom (excluding the radiation interaction) is first diagonalised and then the probability $|b_f(t\to\infty)|^2$ is calculated (11):

$$|b_f(t\to\infty)|^2 = \sum_{\substack{\mu \\ \mu'}} \frac{H_{f\mu} H_{\mu c} H^*_{f\mu'} H^*_{\mu' c}}{[(k_\lambda - k_\nu)^2 + \Gamma^2/4][k_\lambda - E_\mu + E_c + \frac{i}{2}\Gamma][k_\lambda - E_{\mu'} + E_c - \frac{i}{2}\Gamma]} \tag{4-5}$$

where H stands for the radiation interaction (see Appendix A-1). Summation over μ and μ' are over the excited states (the eigenstates of the total Hamiltonian) and E_μ are the energy eigenvalues of the excited states $|\mu\rangle$. The probability $|b_f(t\to\infty)|^2$ is the probability that the atom has absorbed a photon with wave vector $\vec{k}_\nu$ and polarization $\hat{e}_\nu$ during a transition from a ground state $|c\rangle$ to the excited states $|\mu\rangle$ and has emitted a photon with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$ during the transition from the excited states $|\mu\rangle$ to a ground state $|c'\rangle$. In this calculation (Eq.(4-5)), the ground states are considered to be degenerate. The final state $|f\rangle$ is defined as:

$$|f\rangle = |c'\rangle |-k_\nu\rangle_R |+k_\lambda\rangle_R .$$

If all the ground states are equally probable at t = 0, then the total probability that the atom has absorbed a photon with wave vector $\vec{k}_\sigma$ and polarization $\hat{e}_\sigma$ and has emitted a photon with wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$ at $t = \infty$ is given by:

$$\sum_{cc'} |b_f(t=\infty)|^2 = \sum_{\substack{\mu\mu' \\ cc'}} \frac{H_{f\mu} H_{\mu c} H^*_{f\mu'} H^*_{\mu' c}}{[(k_\lambda - k_\sigma)^2 + \frac{\Gamma^2}{4}][k_\lambda - E_\mu + E_c + \frac{i}{2}\Gamma][k_\lambda - E_{\mu'} + E_c - \frac{i}{2}\Gamma]} \tag{4-6}$$

where summations over c and c$'$ are over the ground states.

In order to get the total intensity $I(\Omega_a, \Omega_e, \sigma, \lambda)$ of the scattered beam for a given direction and polarization of the incident and the scattered radiation, the probability in Eq.(4-6) is integrated over all frequencies of the absorbed and the emitted photons. Using the fact that $1/\{(k_\lambda - k_\sigma)^2 + \Gamma^2/4\}$ reduces to $2\pi/\Gamma \; \delta(k_\lambda - k_\sigma)$ for very small Γ and that the product $H_{f\mu} H_{\mu c} H^*_{f\mu'} H^*_{\mu' c}$ can be considered to be constant near the poles of $|b_f(\infty)|^2$, this integration gives:

$$I(\Omega_a, \Omega_e, \sigma, \lambda) \propto \sum_{\substack{\mu\mu' \\ cc'}} \frac{P^\lambda_{c'\mu} P^{\lambda *}_{c'\mu'} P^\sigma_{\mu c} P^{\sigma *}_{\mu' c}}{\gamma + i(E_\mu - E_{\mu'})} \tag{4-7}$$

where $P^\lambda_{c'\mu}$ is the matrix element of $\vec{p}.\hat{e}_\lambda$ between states $|c'\rangle$ and $|\mu\rangle$ (see Appendix A-1) and $\vec{p}$ is the momentum of the electron. This is the well known Briet equation (9).

The intensity $I(\Omega_a, \Omega_e, \sigma, \lambda)$ can be written as:

$$I(\Omega_a, \Omega_e, \sigma, \lambda) \propto \sum_{cc'} \Big[\sum_\mu P^\lambda_{c'\mu} P^{\lambda *}_{c'\mu} P^\sigma_{\mu c} P^{\sigma *}_{\mu c} / \gamma$$

$$+ \sum_{\substack{\mu\mu' \\ \mu \neq \mu'}} \frac{\gamma \, \mathrm{Re}(P^\lambda_{c'\mu} P^{\lambda *}_{c'\mu'} P^\sigma_{\mu c} P^{\sigma *}_{\mu' c}) + (E_\mu - E_{\mu'}) \mathrm{Im}(P^\lambda_{c'\mu} P^{\lambda *}_{c'\mu'} P^\sigma_{\mu c} P^{\sigma *}_{\mu' c})}{(E_\mu - E_{\mu'})^2 + \gamma^2} \tag{4-8}$$

C. Crossing and Anti-crossing Singals for the 2^2P State in Li^7

As an application of the theory developed in the previous section, the intensity of the scattered radiation from a Li^7 atom in an external magnetic field, is calculated. The frequency range of the incident beam is so chosen that only the 1^2S and 2^2P states are involved in the scattering process.

Ignoring the hyperfine structure for the moment, the Hamiltonian of the Lithium atom in the external magnetic field is written as:

$$\mathcal{H} = \mathcal{H}_o + A\vec{L}.\vec{S} + g_s\mu_o\vec{S}.\vec{H} + g_\ell\mu_o\vec{L}.\vec{H} \qquad (4\text{-}9)$$

where $\mathcal{H}_o$ is the Hamiltonian of the atom excluding the fine structure and the magnetic field interactions. The symbols g_s and g_ℓ stand for the electronic spin and orbital Lande g-factors, respectively, μ_o stands for the Bohr magneton, A for the fine structure coupling constant, H for the magnetic field, $\vec{L}$ for the orbital angular momentum operator and S for the spin angular momentum operator. The experimental value of the coupling constant A is approximately 6.75 KMC/sec. (12, p. 13).

If the magnetic field is chosen to be along the Z-direction, then the Hamiltonian $\mathcal{H}$ in Eq. (4-9) reduces to

$$\mathcal{H} = \mathcal{H}_o + A\vec{L}.\vec{S} + g_s\mu_o S_z H + g_\ell\mu_o L_z H \qquad (4\text{-}9a)$$

Due to the presence of the magnetic field interaction terms in this Hamiltonian, the total angular momentum J is no more a good quantum number. However, the magnetic quantum number m_J is a good quantum number.

A representation involving ℓ, s, m_ℓ, and m_s ($|\ell s m_\ell m_s\rangle$) is used to diagonalize the Hamiltonian in Eq.(4-9a). The following eigenstates are obtained as a result of this diagonalization:

$$\begin{aligned}
|\phi_1\rangle &= |1\,\tfrac{1}{2}\,1\,\tfrac{1}{2}\rangle\,,\\
|\phi_2\rangle &= A_0|1\,\tfrac{1}{2}\,0\,\tfrac{1}{2}\rangle + B_0|1\,\tfrac{1}{2}\,1\,-\tfrac{1}{2}\rangle\,,\\
|\phi_3\rangle &= C_0|1\,\tfrac{1}{2}\,-1\,\tfrac{1}{2}\rangle + D_0|1\,\tfrac{1}{2}\,0\,-\tfrac{1}{2}\rangle\,,\\
|\phi_4\rangle &= |1\,\tfrac{1}{2}\,-1\,-\tfrac{1}{2}\rangle\,,\\
|\phi_5\rangle &= -B_0|1\,\tfrac{1}{2}\,0\,\tfrac{1}{2}\rangle + A_0|1\,\tfrac{1}{2}\,1\,-\tfrac{1}{2}\rangle\,,\\
|\phi_6\rangle &= -D_0|1\,\tfrac{1}{2}\,-1\,\tfrac{1}{2}\rangle + C_0|1\,\tfrac{1}{2}\,0\,-\tfrac{1}{2}\rangle\,,
\end{aligned} \tag{4-10}$$

and their corresponding energy eigenvalues are:

$$E_1 = E^0 + A/2 + (g_\ell + g_s/2)\mu_0 H\,,$$

$$E_2 = E^0 - A/4 + 1/2\, g_\ell \mu_0 H + 1/2\left[(g_s - g_\ell)^2 \mu_0^2 H^2 + (g_s - g_\ell)\mu_0 H A + 9A^2/4\right]^{1/2},$$

$$E_3 = E^0 - A/4 - 1/2\, g_\ell \mu_0 H + 1/2\left[(g_s - g_\ell)^2 \mu_0^2 H^2 - (g_s - g_\ell)\mu_0 H A + 9A^2/4\right]^{1/2},$$

$$E_4 = E^0 + A/4 - (g_\ell + g_s/2)\mu_0 H\,,$$

$$E_5 = E^\circ - A/4 + 1/2\, g_l \mu_o H - 1/2[(g_s - g_l)^2 \mu_o^2 H^2$$
$$+ (g_s - g_l)\mu_o H A + 9A^2/4]^{1/2} \,,$$

$$E_6 = E^\circ - A/4 - 1/2\, g_l \mu_o H - 1/2[(g_s - g_l)^2 \mu_o^2 H^2$$
$$- (g_s - g_l)\mu_o H A + 9A^2/4]^{1/2} \tag{4-11}$$

where E^O is the energy of the atom without the fine structure and the magnetic field interactions. The coefficient A_o, B_o, C_o and D_o are defined as:

$$\left.\begin{matrix} A_o \\ B_o \end{matrix}\right\} = \frac{1}{\sqrt{2}}\left(1 \pm \frac{\mu_o H + A/2}{\sqrt{(\mu_o H + A/2)^2 + 2A^2}}\right)^{1/2}$$

and (4-12)

$$\left.\begin{matrix} C_o \\ D_o \end{matrix}\right\} = \frac{1}{\sqrt{2}}\left(1 \pm \frac{\mu_o H - A/2}{\sqrt{(\mu_o H - A/2)^2 + 2A^2}}\right)^{1/2} .$$

When the energies in Eq. (4-11) are plotted as a function of the external magnetic field H, one finds that energy E_4 crosses E_5 at $H = 2A/(3\mu_o)$ and E_6 at $H = A/\mu_o$.

The hyperfine interaction H_D and the electrostatic nuclear quadrupole interaction H_Q are (13):

$$H_D = \alpha\left[\frac{\vec{l} - \vec{s}}{r^3} + 3\frac{(\vec{s}.\vec{r})\,\vec{r}}{r^5}\right]. I + \xi\, \vec{s}.\vec{I} \,, \tag{4-13}$$

and

$$H_Q = -e^2 Q \left[\frac{3I_z^2 - I^2}{4I(2I-1)} \right] \cdot \left(\frac{3\cos^2\theta - 1}{r^3} \right) , \tag{4-14}$$

where Q stands for the nuclear electric quadrupole moment, θ and r are the coordinates of the P electron and α and ξ are constants and have the following experimental values (13).

$$\begin{aligned} \alpha \langle \tfrac{1}{r^3} \rangle &= 13.37 \pm 0.05 \ \text{MC/sec} \\ \xi &= -31.6 \pm 0.7 \ \text{MC/sec} \end{aligned} \tag{4-15}$$

where $\langle 1/r^3 \rangle$ is the average value of $1/r^3$ in the 2P state in Li^7.

The total Hamiltonian $\mathcal{H}_T$ of the atom including the hyperfine and the nuclear quadrupole interaction, is:

$$\mathcal{H}_T = \mathcal{H}_0 + A\vec{L}\cdot\vec{S} + (g_s\vec{S} + g_\ell\vec{L})\cdot\vec{H}\mu_0 + H_D + H_Q \tag{4-16}$$

The presence of the hyperfine interaction in this Hamiltonian, couples the hyperfine states of the same total magnetic quantum number m_f ($m_f = m_\ell + m_s + m_I$). Thus, m_j is no more a good quantum number. Near the high field crossing of the energy levels E_4 and E_6, the coupling between the hyperfine states of $|\phi_4\rangle$ and $|\phi_6\rangle$ is stronger than the coupling with the other hyperfine states. Thus, one can just consider the coupling between the hyperfine states of $|\phi_4\rangle$ and $|\phi_6\rangle$ and can neglect the other couplings without significant error. The intensity of the scattered beam is calculated near the high field crossing of E_4 and E_6.

The following representation is used to diagnolize the total Hamiltonian $\mathcal{H}_T$ in Eq. (4-16):

$$|\phi_i, m_I\rangle = |\phi_i\rangle|3/2\, m_I\rangle ,$$

where the wave vector $|\phi_i\rangle$ are defined in Eq. (4-10). For Li^7 the nuclear spin quantum number I is 3/2.

Considering only the coupling between the hyperfine states of $|\phi_4\rangle$ and $|\phi_6\rangle$ near the high field crossing, the following eigenstates result.

$$\begin{aligned}
|\psi_1\rangle &= C_1|\phi_4, 3/2\rangle + D_1|\phi_6, 1/2\rangle , \\
|\psi_2\rangle &= -D_1|\phi_4, 3/2\rangle + C_1|\phi_6, 1/2\rangle , \\
|\psi_3\rangle &= C_2|\phi_4, 1/2\rangle + D_2|\phi_6, -1/2\rangle , \\
|\psi_4\rangle &= -D_2|\phi_4, 1/2\rangle + C_2|\phi_6, -1/2\rangle , \\
|\psi_5\rangle &= C_3|\phi, -1/2\rangle + D_3|\phi_6, -3/2\rangle , \\
|\psi_6\rangle &= -D_3|\phi, -1/2\rangle + C_3|\phi_6, -3/2\rangle , \\
|\psi_7\rangle &= |\phi_4, -3/2\rangle , \\
|\psi_8\rangle &= |\phi_6, 3/2\rangle .
\end{aligned} \tag{4-17}$$

The coefficients in Eq. (4-17) are defined as

$$\left.\begin{matrix} C_i \\ D_i \end{matrix}\right\} = \frac{1}{\sqrt{2}}\left(1 \pm \frac{\Delta_i}{\sqrt{\Delta_i^2 + 4V_i^2}}\right)^{1/2} ; \quad i = 1, 2, 3 . \tag{4-18}$$

The energy differences Δ_i and the off diagonal matrix elements V_i of the hyperfine interaction H_D, are defined as:

$$\Delta_i = \langle \phi_4, m_I | \mathcal{H}_T | \phi_4, m_I \rangle - \langle \phi_6, m_I - 1 | \mathcal{H}_T | \phi_6, m_I - 1 \rangle \quad (4\text{-}19)$$

and

$$V_i = \langle \phi_4, m_I | H_D | \phi_6, m_I - 1 \rangle \quad (4\text{-}20)$$

where i = 1,2,3 for m_I = 3/2, 1/2 and -1/2, respectively.

The energy eigenvalues of the states $|\Psi_j\rangle$ are:

$$\left.\begin{matrix} E_1' \\ E_2' \end{matrix}\right\} = \frac{\langle \phi_4, 3/2 | \mathcal{H}_T | \phi_4, 3/2 \rangle + \langle \phi_6, 1/2 | \mathcal{H}_T | \phi_6, 1/2 \rangle}{2} \pm \sqrt{\Delta_1^2 + 4V_1^2} \;, \quad (4\text{-}21)$$

$$\left.\begin{matrix} E_3' \\ E_4' \end{matrix}\right\} = \frac{\langle \phi_4, 1/2 | \mathcal{H}_T | \phi_4, 1/2 \rangle + \langle \phi_6, -1/2 | \mathcal{H}_T | \phi_6, -1/2 \rangle}{2} \pm \sqrt{\Delta_2^2 + 4V_2^2} \;, \quad (4\text{-}22)$$

$$\left.\begin{matrix} E_5' \\ E_6' \end{matrix}\right\} = \frac{\langle \phi_4, -1/2 | \mathcal{H}_T | \phi_4, -1/2 \rangle + \langle \phi_6, -3/2 | \mathcal{H}_T | \phi_6, -3/2 \rangle}{2} \pm \sqrt{\Delta_3^2 + 4V_3^2} \;. \quad (4\text{-}23)$$

$$\begin{aligned} E_7' &= \langle \phi_4, -3/2 | \mathcal{H}_T | \phi_4, -3/2 \rangle \;, \\ E_8' &= \langle \phi_6, 3/2 | \mathcal{H}_T | \phi_6, 3/2 \rangle \;, \end{aligned} \quad (4\text{-}24)$$

where the subscript on E' corresponds to the subscript of the eigenstate $|\psi\rangle$. Using the matrix elements of H_D and H_Q as calculated in Appendix D, the following expressions are obtained for the diagonal matrix elements of the total Hamiltonian:

$$\langle \phi_4, m_I | \mathcal{H}_T | \phi_4, m_I \rangle = E^o + A/2 - 2\mu_o H$$
$$- m_I \left(\tfrac{4}{5} \alpha \langle \tfrac{1}{r^3} \rangle + \tfrac{1}{2} \xi \right) + \tfrac{b}{4} \left(m_I^2 - \tfrac{5}{4} \right)$$

and

$$\langle \phi_6, m_I | \mathcal{H}_T | \phi_6, m_I \rangle = E^o - (D_o^2/2 + \sqrt{2}\, C_o D_o) A$$
$$- m_I\, \alpha \langle 1/r^3 \rangle (6 D_o^2 + 2 C_o^2 + \sqrt{2} . 3 C_o D_o)/5 + \tfrac{1}{2}(D_o^2 - C_o^2) \xi m_I$$
$$- C_o^2 \mu_o H + b(D_o^2 - 2 C_o^2)/4 \cdot (m_I^2 - 5/4) . \qquad (4\text{-}25)$$

The off-diagonal matrix elements of H_D as calculated in Appendix D, are:

$$V_i = \langle \phi_4, m_I | H_D | \phi_6, m_I - 1 \rangle = \tfrac{1}{2} \left[\left(\tfrac{7}{5\sqrt{2}} C_o - \tfrac{1}{5} D_o \right) \alpha \langle \tfrac{1}{r^3} \rangle \right.$$
$$\left. - D_o \xi \right] \cdot \sqrt{(5/2 - m_I)(3/2 + m_I)} \qquad (4\text{-}26)$$

where i = 1,2,3 for m_I = 3/2, 1/2 and -1/2 respectively.

If the off-diagonal matrix elements of H_D are assumed to be zero, then there is no coupling between the states of the same total magnetic quantum number m_f, and the states $|\phi_4, m_I\rangle$ and $|\phi_6, m_I\rangle$ are the eigenstates of $\mathcal{H}_T$. For this case (V_i = o), the energies of the states $|\phi_4, m_I\rangle$ and $|\phi_6, m_I\rangle$ are plotted in Fig. 4-2 as a function of the external magnetic field H. There are two sets of levels, one originating from the $^2P_{3/2-3/2}$ state and the

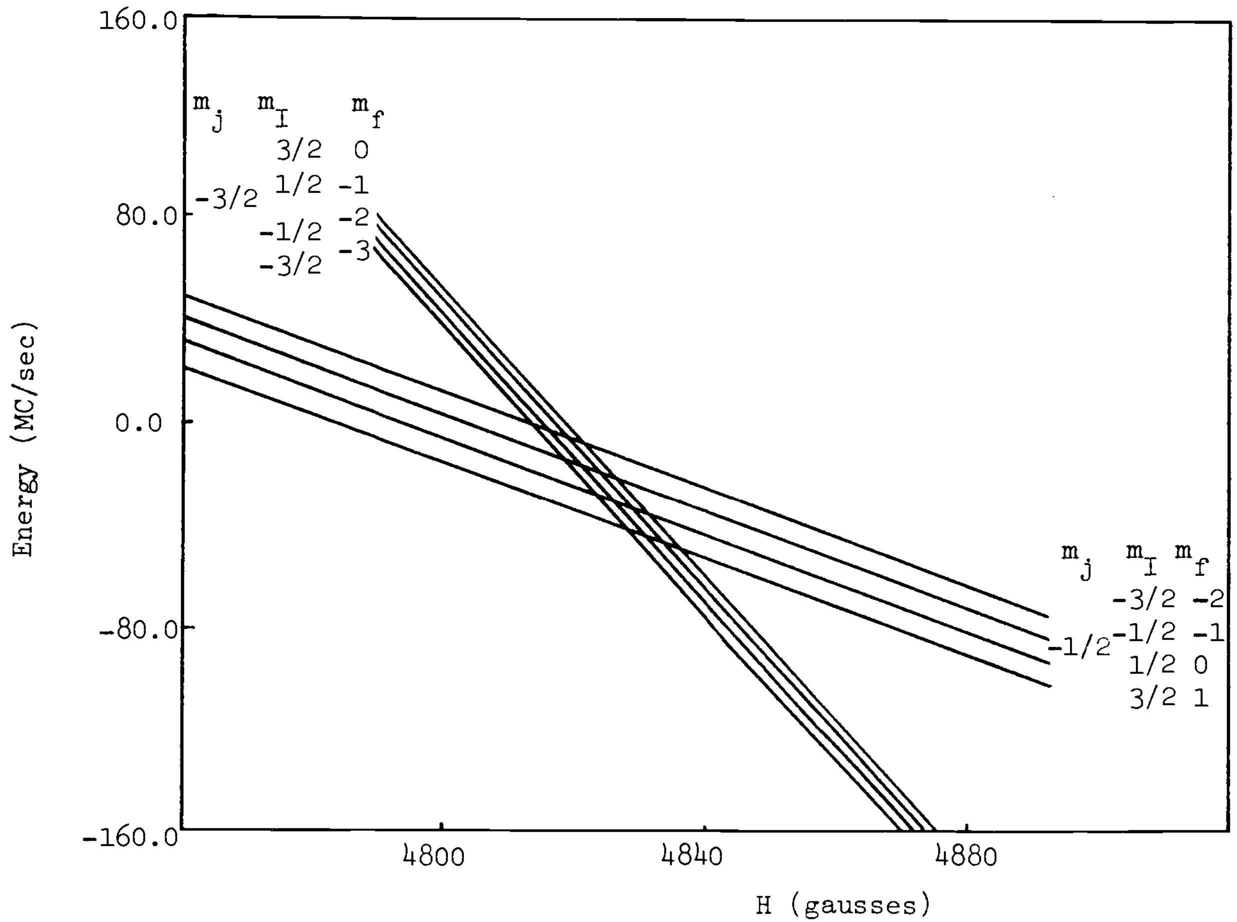

Fig. 4-2. The hyperfine levels of $2^2P_{3/2-3/2}$ and $2^2P_{1/2-1/2}$ in Li^7 as a function of an external magnetic field H, without considering the coupling between the hyperfine states.

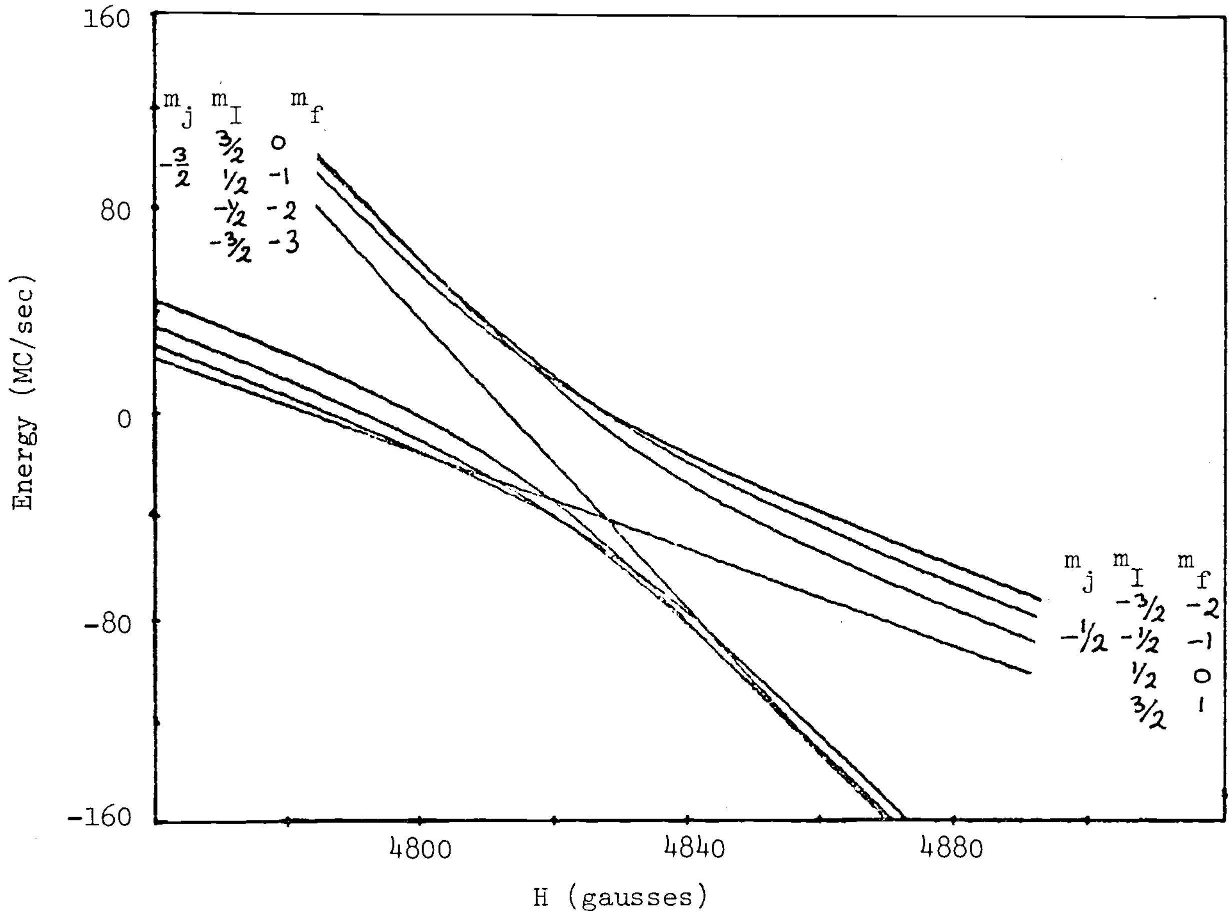

Fig. 4-3. The hyperfine levels of $2^2P_{3/2-3/2}$ and $2^2P_{1/2-1/2}$ in Li^7 as a function of an external magnetic field H. The coupling between the different hyperfine states is considered here.

other from the $^2P_{1/2-1/2}$ state. These two sets of states cross each other near H = 4825 gausses. In order to get a "crossing" signal in the scattered beam, the states which cross each other must decay to a common ground state. There are four such crossings of interest where the two levels have the same m_I.

If the off-diagonal matrix elements of H_D are considered to be non zero, the two states of the same m_f are coupled and the crossings mentioned earlier no longer exist. The energy **eigenvalues** for this case ($V_i \neq 0$) are plotted in Fig. 4-3 as a function of the external magnetic field H. There are three pairs of states which anticross and there are six crossings that contribute to the signal. These crossings are far apart. The curves in Fig. 4-3 are quite different from the ones presented by Wieder and Eck (7). According to their graph only two crossings contribute to the signal.

From Eq. (4-8), the intensity of the scattered beam for a given direction and polarization of the incident and the scattered beam, is

$$I(\Omega_a, \Omega_e, \alpha, \lambda) \propto \sum_{cc'} \Big[\sum_{\mu} P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu} P^{\alpha}_{\mu c} P^{\alpha *}_{\mu c} / \gamma + \frac{1}{2} \sum_{\substack{\mu\mu' \\ \mu \neq \mu'}} \frac{2\gamma \, \mathrm{Re}(P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu'} P^{\alpha}_{\mu c} P^{\alpha *}_{\mu' c}) + 2(E'_{\mu} - E'_{\mu'}) \, \mathrm{Im}(P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu'} P^{\alpha}_{\mu c} P^{\alpha *}_{\mu' c})}{(E'_{\mu} - E'_{\mu'})^2 + \gamma^2} \Big] \tag{4-27}$$

where the summations over μ and μ' are over the excited states as defined in Eq. (4-17) and the summation over c and c$'$ are over the ground states. The following states are the ground states of Li^7:

$$|C_j\rangle = |0 \, 1/2 \, 0 \, 1/2\rangle \, |3/2 \; m_I\rangle$$

wher j = 1,2,3,4 for m_I = 3/2, 1/2,-1/2 and -3/2, respectively, and

$$|C_j\rangle \quad = \quad |0\ {}^1\!/\!_2\ 0\ -{}^1\!/\!_2\rangle\,|{}^3\!/\!_2\ m_I\rangle \ ,$$

where j= 5,6,7,8 for m_I = 3/2,1/2,-1/2 and -3/2, respectively. It is assumed that there is no coupling between the different hyperfine states of the ground states.

Substituting in Eq.(4-27), the matrix elements $p^{\lambda}_{c'\mu}$, $p^{\lambda*}_{c'\mu'}$, $p^{\sigma}_{\mu c}$ and $p^{\sigma*}_{\mu' c}$ in terms of the states $|\phi_4, m_I\rangle$ and $|\phi_6, m_I\rangle$, using the selection rule $\Delta m_I = 0$ ($p^{\lambda}_{c\mu} = 0$ if $|c\rangle$ and $|\mu\rangle$ have different m_I) and regrouping the terms with V_i in the numerator, one obtains the following expression for the anticrossing signals (after some tedious algebraic manipulations):

$$S_A \propto (-1) \sum_{i=1,2,3} 2V_i^2 \left(\sum_c |p^{\lambda}_{ca_i}|^2 - \sum_c |p_{cb_i}|^2 \right)$$

$$\times \quad \frac{\left(\sum_c |p^{\sigma}_{a_i c}|^2 - \sum_c |p^{\sigma}_{b_i c}|^2 \right)}{\Delta_i^2 + 4V_i^2 + \gamma^2} \qquad (4\text{-}28)$$

where the states $|a_i\rangle$ and $|b_i\rangle$ stand for a set of two states which are coupled by H_D. In terms of $|\phi_4, m_I\rangle$ and $|\phi_6, m_I\rangle$, the states $|a_i\rangle$ and $|b_i\rangle$ are:

$$|a_i\rangle = |\phi_4, m_I\rangle \ ,$$

$$|b_i\rangle = |\phi_6, m_I - 1\rangle \ ,$$

where i = 1,2,3 for m_I = 3/2, 1/2, and -1/2, respectively.

There are four terms of the form $|\langle c|\hat{P}^{\lambda}|\phi_4, m_I\rangle|^2 \cdot |\langle c|\hat{P}^{\sim}|\phi_4, m_I\rangle|^2$ and four of the form $|\langle c|\hat{P}^{\lambda}|\phi_i, m_I\rangle|^2 | \langle c|\tilde{P}|\phi_i, m_I\rangle|^2$ in the total intensity I $(\Omega_a, \Omega_e, \sim, \lambda)$. These terms provide a very slowely varying signal as a function of the external magnetic field. They are not discussed here and therefore are absorbed in the background signal. The remaining terms in Eq.(4-27) give the crossing signal:

$$S_c = \sum_{\mu}\sum_{\mu'}\sum_{cc'} \frac{\gamma\, Re\,(P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu'} P^{\sim}_{\mu c} P^{\sim *}_{\mu' c}) + (E'_{\mu} - E'_{\mu'})\, Im\,(P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu'} P^{\sim}_{\mu c} P^{\sim *}_{\mu' c})}{(E_{\mu} - E_{\mu'})^2 + \gamma^2/4} \tag{4-29}$$

where

μ = 1 for μ' = 3,4,5,6,7,8

μ = 2 for μ' = 3,4,5,6,7,8

μ = 3 for μ' = 5,6,7,8

μ = 4 for μ' = 5,6,7,8

μ = 5 for μ' = 7,8

μ = 6 for μ' = 7,8

μ = 7 for μ' = 8 .

These values of μ and μ' are the subscript of the eigenstates $|\psi\rangle$ defined in Eq.(4-17).

Calculating the product $P^{\lambda}_{c'\mu} P^{\lambda *}_{c'\mu'} P^{\sim}_{\mu c} P^{\sim *}_{\mu' c}$ in terms of the orbital states $|l\, m_l\rangle$ (see Appendix E) and substituting the result into Eq. (4-29), one obtains:

$$S_c \propto C_0^2 \left[D_1^2 C_2^2 \frac{\gamma\, Re(f) + (E_1' - E_3')\, Im(f)}{(E_1' - E_3')^2 + \gamma^2} + D_1^2 D_2^2 \frac{\gamma\, Re(f) + (E_1' - E_4')\, Im(f)}{(E_1' - E_4')^2 + \gamma^2} \right.$$

$$+ C_1^2 \frac{\gamma^2 Re(f) - (E_1' - E_8') Im(f)}{(E_1' - E_8')^2 + \gamma^2} + C_1^2 C_2^2 \frac{\gamma Re(f) + (E_2' - E_3') Im(f)}{(E_2' - E_3')^2 + \gamma^2}$$

$$+ C_1^2 D_2^2 \frac{\gamma Re(f) + (E_2' - E_4') Im(f)}{(E_2' - E_4')^2 + \gamma^2} + D_1^2 \frac{\gamma Re(f) - (E_2' - E_8') Im(f)}{(E_2' - E_8')^2 + \gamma^2}$$

$$+ C_3^2 D_2^2 \frac{\gamma Re(f) + (E_3' - E_5') Im(f)}{(E_3' - E_5')^2 + \gamma^2} + D_3^2 D_2^2 \frac{\gamma Re(f) + (E_3' - E_6') Im(f)}{(E_3' - E_6')^2 + \gamma^2}$$

$$+ C_3^2 C_2^2 \frac{\gamma Re(f) + (E_4' - E_5') Im(f)}{(E_4' - E_5')^2 + \gamma^2} + C_2^2 D_3^2 \frac{\gamma Re(f) + (E_4' - E_6') Im(f)}{(E_4' - E_6')^2 + \gamma^2}$$

$$+ D_3^2 \frac{\gamma Re(f) + (E_5' - E_7') Im(f)}{(E_5' - E_7')^2 + \gamma^2} + C_3^2 \frac{\gamma Re(f) + (E_6' - E_7') Im(f)}{(E_6' - E_7')^2 + \gamma^2} \Bigg]$$

(4-30)

where

$$f = \langle 00|\vec{p}\cdot\hat{e}_\lambda|10\rangle\langle 1\,{-1}|\vec{p}\cdot\hat{e}_\lambda|00\rangle\langle 10|\vec{p}\cdot\hat{e}_\sigma|00\rangle\langle 00|\vec{p}\cdot\hat{e}_\sigma|1\,{-1}\rangle$$

(4-31)

The energies E_j' are defined in Eq.(4-21) to Eq.(4-24) and the coefficients C_i and D_i in Eq.(4-18). The vector $\vec{p}$ is the momentum of the valence electron in Li^7 and $\hat{e}_\sigma$ and $\hat{e}_\lambda$ define the direction and polarization of the incident and the scattered beams, respectively.

From Eq.(4-28) and Eq.(4-30), the anticrossing and crossing signals are calculated for the following experimental situation.

The incident beam is plane polarized and is along the x-direction. The scattered beam is also plane polarized and is along the y-direction. The plane of polarization of the incident beam makes an angle θ_a and the plane of polarization of the scattered beam makes an angle θ_e with the z-axis, respectively. The results are:

$$S_A \propto (-1)\, C_0^4\, (1-3\cos^2\theta_e)(1-3\cos^2\theta_a) \sum_{i=1,2,3} V_i^2/(\Delta_i^2+4V_i^2+\gamma^2) \tag{4-32}$$

and

$$\begin{aligned} S_C \propto (-1)\, C_0^2 \sin 2\theta_e \sin 2\theta_a \Bigg[& \frac{D_1^2 C_2^2 (E_1'-E_3')}{(E_1'-E_3')^2+\gamma^2} \\ & + D_1^2 D_2^2 \frac{(E_1'-E_4')}{(E_1'-E_4')^2+\gamma^2} + C_1^2 \frac{(E_8'-E_1')}{(E_8'-E_1')^2+\gamma^2} \\ & + C_1^2 C_2^2 \frac{(E_2'-E_3')}{(E_2'-E_3')^2+\gamma^2} + C_1^2 D_2^2 \frac{(E_2'-E_4')}{(E_2'-E_4')^2+\gamma^2} \\ & + D_1^2 \frac{(E_8'-E_2')}{(E_8'-E_2')^2+\gamma^2} + C_3^2 D_2^2 \frac{(E_3'-E_5')^2}{(E_3'-E_5')^2+\gamma^2} \\ & + D_3^2 D_2^2 \frac{(E_3'-E_6')}{(E_3'-E_6')^2+\gamma^2} + C_3^2 C_2^2 \frac{(E_4'-E_5')}{(E_4'-E_5')^2+\gamma^2} \\ & + C_2^2 D_3^2 \frac{(E_4'-E_6')}{(E_4'-E_6')^2+\gamma^2} + D_3^2 \frac{(E_5'-E_7')}{(E_5'-E_7')^2+\gamma^2} \\ & + C_3^2 \frac{(E_6'-E_7')}{(E_6'-E_7')^2+\gamma^2} \Bigg] . \end{aligned} \tag{4-33}$$

From Eq.(4-32), one finds that the anticrossing signal vanishes for either $\theta_a = \cos^{-1}(1/\sqrt{3})$ or $\theta_e = \cos^{-1}(1/\sqrt{3})$. Similarly from Eq. (4-33), the crossing signal is found to vanish if $\theta_a = n\pi/2$ or $\theta_e = m\pi/2$, where n and m are integers. Thus, there is no crossing signal if the polaroids are oriented parallel, perpendicular or anti-parallel to the magnetic field. These signals are plotted in Fig. 4-4 and Fig. 4-5 as a function of the external magnetic field. The anticrossing signal is Lorentizian and the crossing signal is dispersion type. In order to compare these signals with the experimental signals obtained by Wieder and Eck (7), the derivative of the signals are plotted in Fig. 4-6 and Fig. 4-7 as a function of H. It is observed that the two signals are in good agreement with the experimental signals (Compare Fig. 4-6 with Fig. 4-8 and Fig. 4-7 with Fig. 4-9). In Fig. 4-6, the separation between the maximum and minimum of the derivative signal $\frac{dS_A}{dH}$ is approximately 35 gausses which is the same as that obtained by Eck, Foldy and Wieder (2). The form of the derivative signal $\frac{dS_c}{dH}$ in Fig. 4-7 is similar to that of the experimental signal in Fig. 4-9. The position of the central minimum is near the center of the anticrossing signal as pointed out by Wieder and Eck (7). The separation between the prominant maximum and the minimum is of the order of 36 gausses. Wieder and Eck have not quoted the experimental value for this separation.

It is interesting to note that the crossing and anticrossing signals are observed even if the incident and the scattered beams are unpolarized. The following experimental geometry is considered

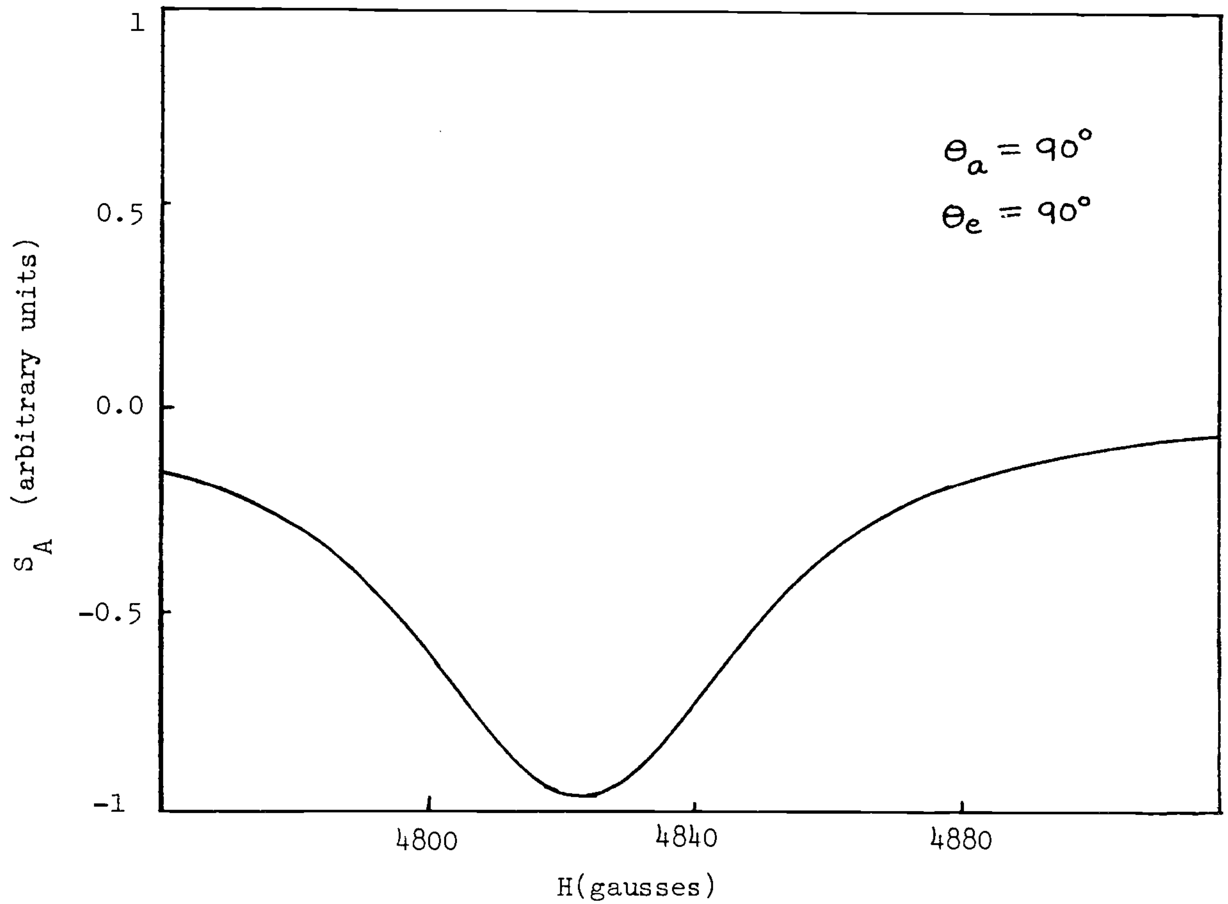

Fig. 4-4. Anticrossing signal in Li^7 as a function of an external magnetic field H. The incident and the scattered beams are along the x- and y-axes and their planes of polarization make angles θ_a and θ_e with the z-axis, respectively.

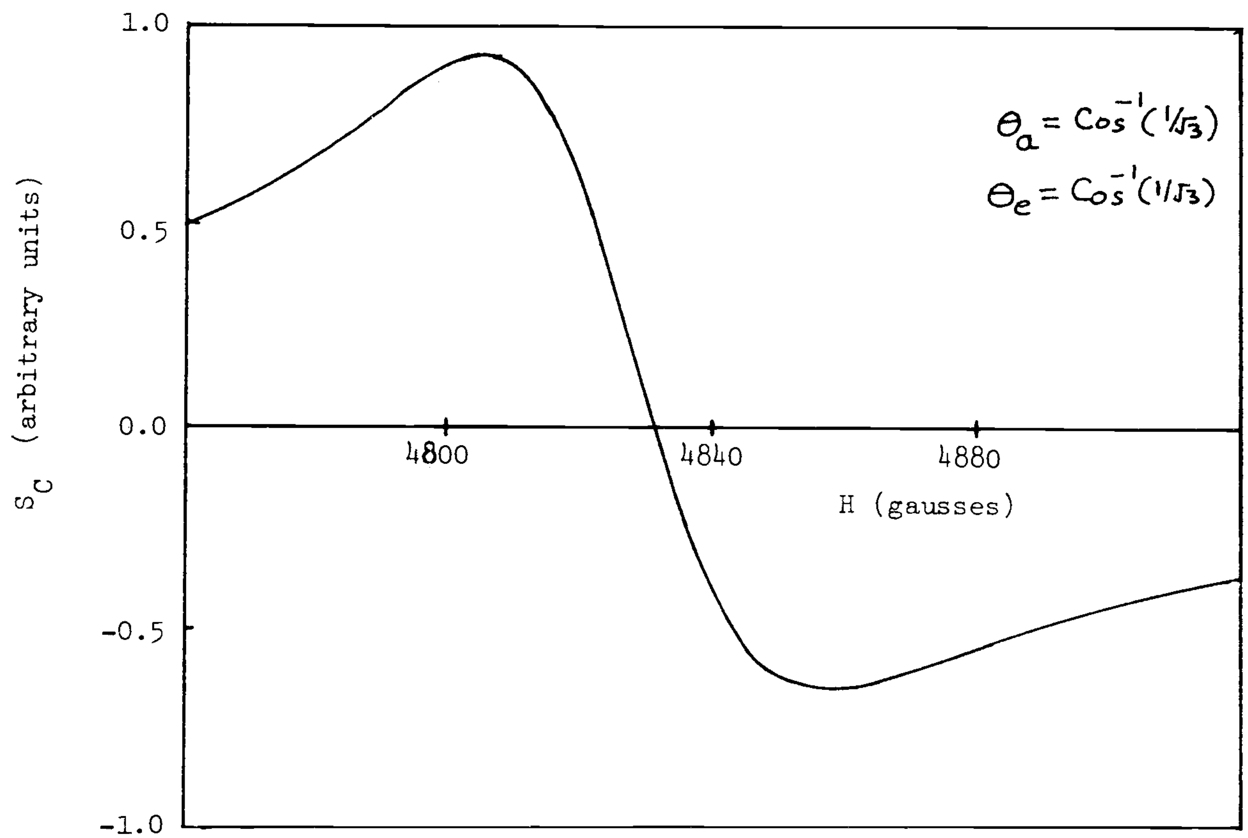

Fig. 4-5. Crossing signal in Li^7 as a function of an external magnetic field H. The incident and the scattered beams are along the x- and y-axes and their planes of polarization make angles θ_a and θ_e with the z-axis, respectively.

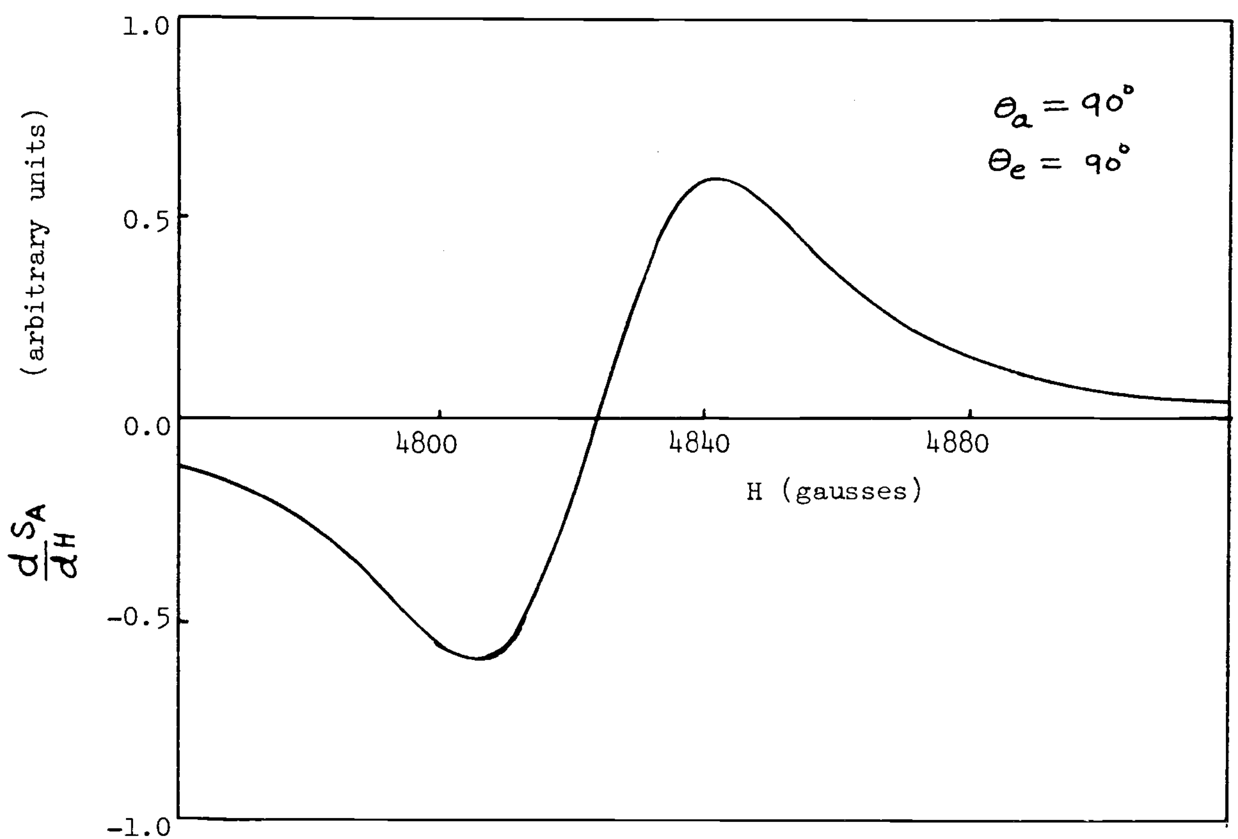

Fig. 4-6. Derivative of the anticrossing signal in Li^7 as a function of the external magnetic field H. The incident and the scattered beams are along the x- and y-axes and their planes of polarization make angles θ_a and θ_e with the z-axis, respectively.

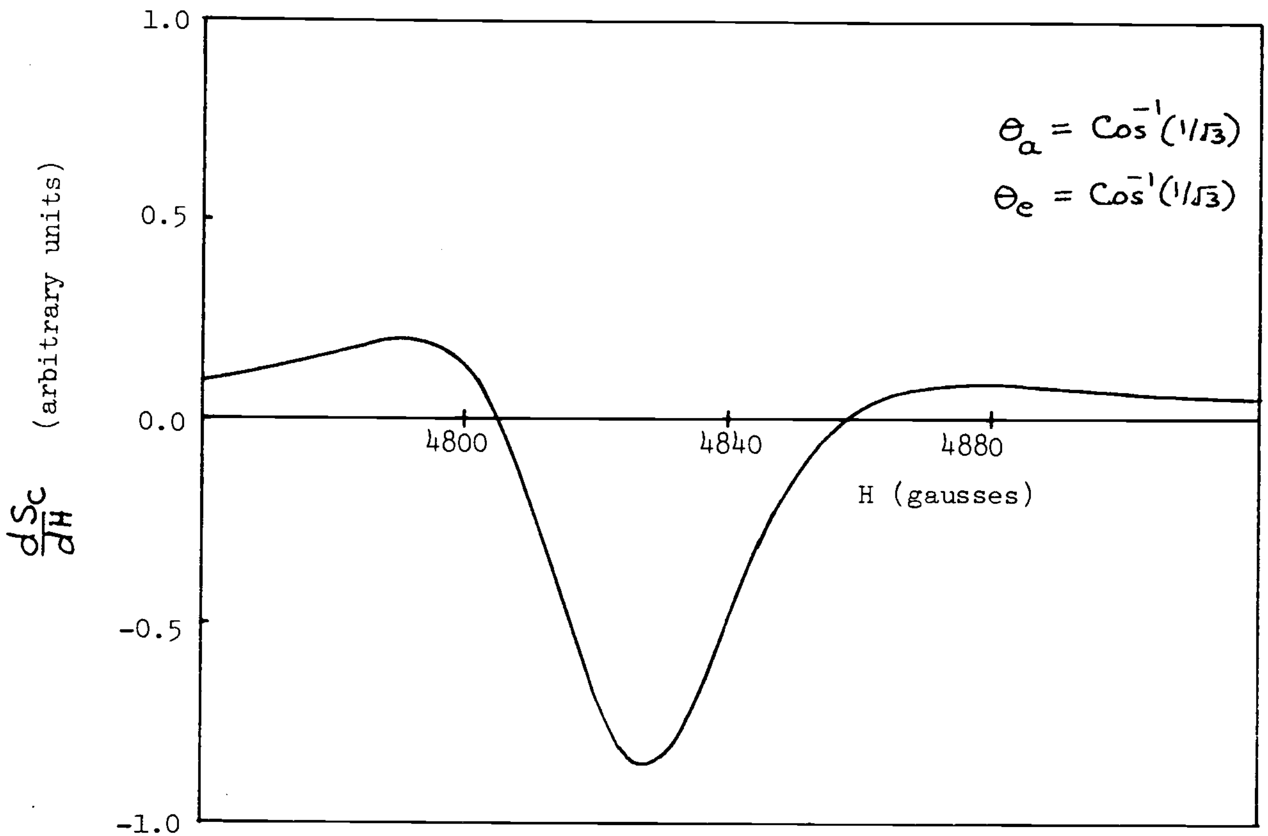

Fig. 4-7. Derivative of the crossing signal in Li^7 as a function of the external magnetic field H. The incident and the scattered beams are along the x-and y-axes and their planes of polarization make angles θ_a and θ_e with the z-axis, respectively.

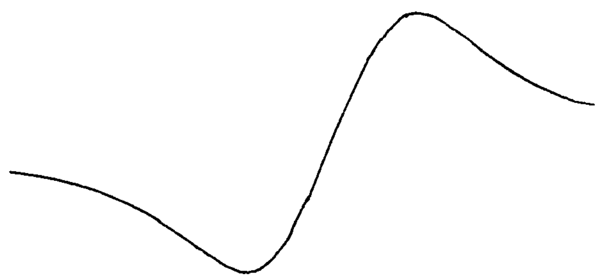

Fig. 4-8. The derivative of the anticrossing signal in the 2^2P term of Li^7 as obtained by Wieder and Eck (7) experimentally.

Fig. 4-9. The derivative of the crossing signal in the 2^2P term of Li^7 as obtained by Wieder and Eck (7) experimentally.

for this case. The incident and the scattered beams are unpolarized and they make angles θ_1 and θ_2 with the z-axis, respectively (see Fig. 4-10).

The anticrossing signal in this case has the same functional dependence in H and the same angular dependence in θ_1 and θ_2 as discussed earlier for the polarized beam, except that θ_a and θ_e are now replaced by θ_1 and θ_2 , respectively. This signal is independent of the azimuthal angle of the incident and the scattered beams.

The following expression is obtained for the crossing signal

$$
\begin{aligned}
S_c \propto C_0^2 \sin 2\theta_1 \sin 2\theta_2 \Big[& D_1^2 C_2^2 \frac{\gamma P + Q(E_1'-E_3')}{(E_1'-E_3')^2 + \gamma^2} \\
& + D_1^2 D_2^2 \frac{\gamma P + Q(E_1'-E_4')}{(E_1'-E_4')^2 + \gamma^2} + C_1^2 \frac{\gamma P - Q(E_1'-E_8')}{(E_1'-E_8')^2 + \gamma^2} \\
& + C_1^2 C_2^2 \frac{\gamma P + Q(E_2'-E_3')}{(E_2'-E_3')^2 + \gamma^2} + C_1^2 D_2^2 \frac{\gamma P + Q(E_2'-E_4')}{(E_2'-E_4')^2 + \gamma^2} \\
& + D_1^2 \frac{\gamma P - Q(E_2'-E_8')}{(E_2'-E_8')^2 + \gamma^2} + C_3^2 D_2^2 \frac{\gamma P + Q(E_3'-E_5')}{(E_3'-E_5')^2 + \gamma^2} \\
& + D_3^2 D_2^2 \frac{\gamma P + Q(E_3'-E_6')}{(E_3'-E_6')^2 + \gamma^2} + C_3^2 C_2^2 \frac{\gamma P + Q(E_4'-E_5')}{(E_4'-E_5')^2 + \gamma^2} \\
& + C_3^2 D_2^2 \frac{\gamma P + Q(E_4'-E_6')}{(E_4'-E_6')^2 + \gamma^2} + D_3^2 \frac{\gamma P + Q(E_5'-E_7')}{(E_5'-E_7')^2 + \gamma^2} \\
& + C_3^2 \frac{\gamma P + Q(E_6'-E_7')}{(E_6'-E_7')^2 + \gamma^2} \Big] \qquad (4\text{-}34)
\end{aligned}
$$

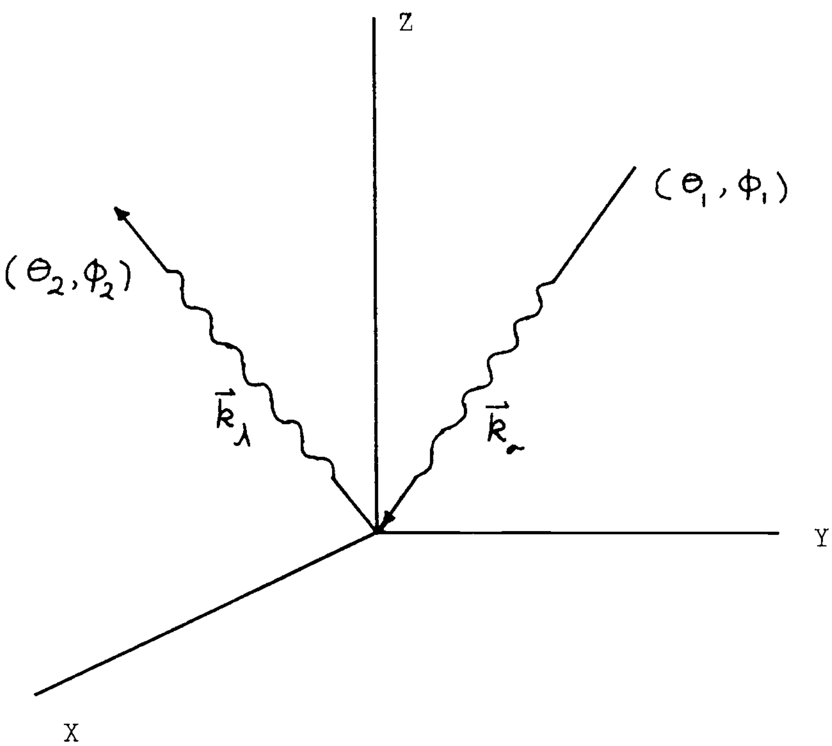

Fig. 4-10. The experimental geometry.

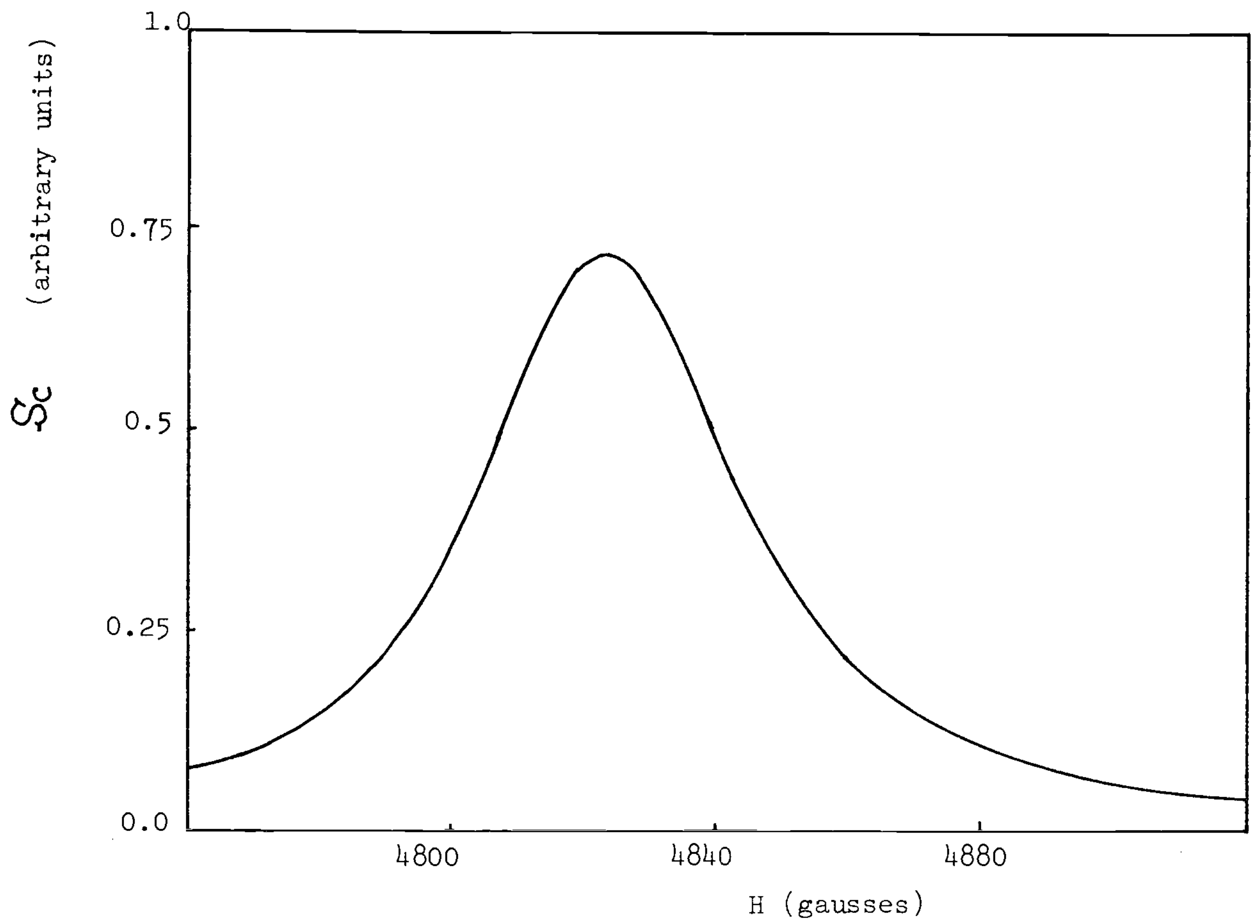

Fig. 4-11. Crossing signal in Li^7 as a function of the external magnetic field H. The incident and the scattered beams are unpolarized and are in the x-z plane.

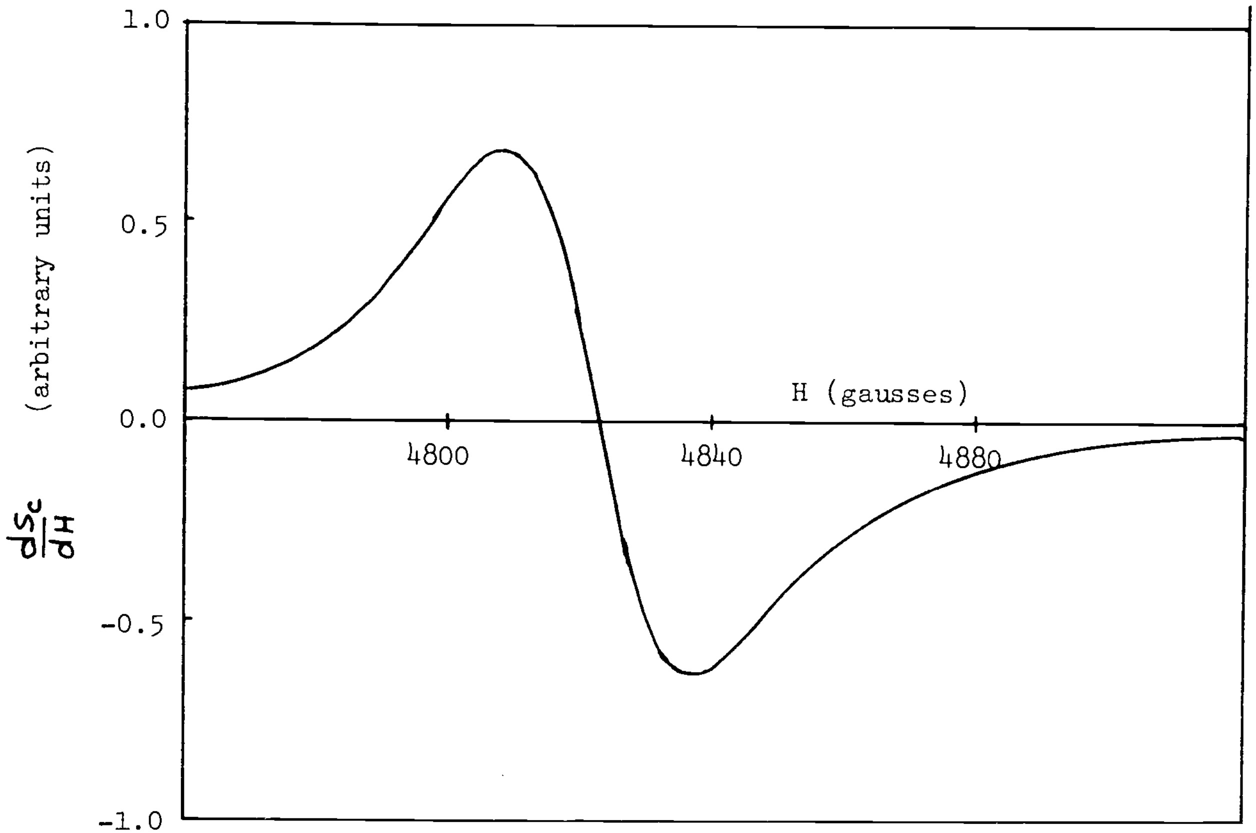

Fig. 4-12. Derivative of the crossing signal in Li^7 as a function of the external magnetic field H. The incident and the scattred beams are unpolarized and are in the x-z plane.

where

$$P + iQ = e^{i(\phi_2 - \phi_1)} \quad .$$

This signal depends on the difference of the azimuthal angles of the incident and the scattered beams. If $\phi_2 - \phi_1$ is $\pi/2$ or $3\pi/2$, the signal is pure dispersion. If $\phi_2 - \phi_1$ is 0 or π then the signal is pure lorentizian. The signal vanishes for $\theta_1 = n\pi/2$ or $\theta_2 = m\pi/2$ where n and m are integers. The signal S_c in Eq.(4-34) is plotted in Fig. 4-11 as a function of the external magnetic field. The incident and the scattered beams are in the x-z plane ($\phi_1 = \phi_2 = 0$). This signal is pure lorentzian and has a maximum near 4826 gausses. The derivative signal $\frac{dS_c}{dH}$ is also plotted in Fig. 4-12. The separation between the maximum and the minimum in this signal is approximately 28 gausses.

BIBLIOGRAPHY

1. Colegrove, F. D., P. A. Franken, R. R. Lewis, and R. H. Sands. Novel method of spectroscopy with applications to precision fine structure measurements. Physical Review Letters 3:420-422. November 1, 1959.

2. Eck, T. G., L. L. Foldy, and H. Wieder. Observation of "anticrossing" in optical resonance fluorescence. Physical Review Letters 10:239-242. March 15, 1963.

3. Himmell, L. C., and P. R. Fontana. Resonance scattering of light from atomic Hydrogen. Physical Review 162:23-28. October, 1967.

4. Hearn, D. Dwight, and P. R. Fontana. Effects of atomic interactions on the absorption and emission of radiation. The Journal of Chemical Physics 51:1871-1879. September 1, 1969.

5. Heitler, W. and S. T. Ma. Quantum theory of radiation damping for discrete states. Proceedings of the Royal Irish Academy 52:109-125. February, 1949.

6. Weisskopf, V. and E. Wigner. Berechnung der natürlichen linienbreite auf grund der diracschen lichttheorie. Zeitschrift für Physik 63:54-73. July, 1930.

7. Wieder, H. and T. G. Eck. "Anticrossing" signals in resonance fluorescence. Physical Review 153: 103-112. January, 1967.

8. Heitler, W. The quantum theory of radiation. 3d ed. London, Oxford University Press, 1960. 430 p.

9. Breit, G. Quantum theory of dispersion. Parts VI and VII. Reviews of Modern Physics 5:91-140. April, 1933.

10. Bethe, Hans A. and Edwin E. Salpeter. Quantum mechanics of one- and two- electron atoms. New York, Academic Press, 1957. 368 p.

11. Himmell, L. C. Cross-over signals in atomic Hydrogen. Doctoral dissertation. Ann Arbor, University of Michigan, 1965. 215 numb. leaves.

12. Di Lavore III, Philip. A measurement of the fine and hyperfine structures of the 2^2P states of Li^7. Doctoral dissertation. Ann Arbor, University of Michigan, 1967. 89 numb. leaves.

13. Brog, K. C., T. G. Eck and H. Wieder. Fine and hyperfine structure of the 2^2P term of Li^6 and Li^7. Physical Review 153:91-103. January, 1967.

14. Fontana, Peter R. Spin-orbit and spin-spin interactions in diatomic molecules. I. Fine structure of H_2. Physical Review 125: 220-228. January, 1962.

15. Rose, M. E. Elementary theory of angular momentum. New York, John Wiley & Sons, Inc., 1957, 248 p.

16. Lamb, Willis E. Jr. Fine structure of the Hydrogen atom. III. Physical Review 85:259-276. January 15, 1952.

17. Lamb, Willis E. Jr. and Robert C. Retherford. Fine structure of the Hydrogen atom. Part II. Physical Review 81:222-232. January 15, 1951.

APPENDICES

APPENDIX A

1. Matrix Elements of H

The perturbation involving the interaction of the radiation field with the atom is

$$H = e\sum_{k_\sigma}\left(\frac{2\pi}{L^3 k_\sigma}\right)^{\frac{1}{2}}\left[a(k_\sigma)\,e^{i\vec{k}_\sigma\cdot\vec{r}} + a^\dagger(k_\sigma)\,e^{-i\vec{k}_\sigma\cdot\vec{r}}\right]\hat{e}_\sigma\cdot\vec{p} \tag{A-1}$$

where the summation over k_σ is over frequency, direction and polarization of the radiation field. The operators $a(k_\sigma)$ and $a^\dagger(k_\sigma)$ are the anihilation and creation operators, respectively, for a photon with wave vector $\vec{k}_\sigma$ and polarization $\hat{e}_\sigma$. The vectors $\vec{r}$ and $\vec{p}$ are the position and momentum vectors, respectively, of the electron with respect to the center of mass of the atom. The radiation field is considered to be enclosed in a box of volume L^3.

In the dipole approximation ($k_\sigma r \ll 1$);

$$e^{i\vec{k}_\sigma\cdot\vec{r}} = 1$$

and the matrix elements H_{fi}, H_{fj}, H_{oi} and H_{oj} reduce to

$$\begin{aligned} H_{fi} &= \langle f|H|i\rangle \\ &= \langle c|\langle k_\lambda|_R\langle -k_\sigma|H|-k_\sigma\rangle_R|a\rangle \\ &= e\,(2\pi/(L^3 k_\lambda))^{1/2}\,p_{ca}^{\lambda}\,\{n(k_\lambda)+1\}^{1/2} \end{aligned} \tag{A-2}$$

$$H_{fj} = e\,(2\pi/(L^3 k_\lambda))^{1/2}\,p_{cb}^{\lambda}\,\{n(k_\lambda)+1\}^{1/2}$$

$$H_{oi} = e\,(2\pi/(L^3 k_\sigma))^{1/2}\, p^{\sigma}_{ca} \cdot \sqrt{n(k_\sigma)}$$

and (A-3)

$$H_{oj} = e\,(2\pi/(L^3 k_\sigma))^{1/2}\, p^{\sigma}_{cb} \sqrt{n(k_\sigma)}$$

where $n(k_\lambda)$ and $n(k_\sigma)$ are the occupation numbers of the emitted and the absorbed photons, respectively, and

$$p^{m}_{c\ell} = \langle c|\,\hat{e}_m \cdot \vec{p}\,|\ell\rangle \;; \quad m = \lambda, \sigma \;;\; \ell = a, b. \qquad \text{(A-4)}$$

Usually, the spontaneous emission process dominates over the induced one, which means that $n(k_\lambda) \ll 1$. Thus, one can neglect the occupation number $n(k_\lambda)$ compared to one in the matrix elements H_{fi} and H_{fj} and they therefore reduce to

$$H_{fi} = e\sqrt{\frac{2\pi}{L^3 k_\lambda}} \cdot p^{\lambda}_{ca}$$

and (A-5)

$$H_{fj} = e\sqrt{\frac{2\pi}{L^3 k_\lambda}} \cdot p^{\lambda}_{cb} \; .$$

2. Evaluation of Υ_{ii}

In Eq.(2-33), Υ_{ii} is defined as

$$-\frac{i}{2}\Upsilon_{ii}(E) = \sum_f H_{if}\cdot H_{fi}\,\varsigma(E-E_f') .$$

using Eq.(2-28), the real part of Υ_{ii} is written as

$$Re(\Upsilon_{ii}(E)) = 2\pi\sum_f H_{if}H_{fi}\,\delta(E-E_f') . \qquad \text{(A-6)}$$

for a continuous distribution of frequencies, the summation is replaced by an integration:

$$\sum_f \longrightarrow \left(\frac{L}{2\pi}\right)^3 \sum_\lambda \int_0^\infty k_\lambda^2 dk_\lambda \int_0^\pi \sin\theta_e\, d\theta_e \int_0^{2\pi} d\phi_e \qquad \text{(A-7)}$$

where θ_e and ϕ_e are the polar and azimuthal angles of the wave vector $\vec{k}_\lambda$. The summation over λ is over the polarization of the emitted radiation. Thus, using Eq.(A-2) and Eq.(A-7), one gets

$$Re(\Upsilon_{ii}(E)) = \frac{e^2}{2\pi}(E-E_c'+k_r)\sum_\lambda \int_0^\pi\int_0^{2\pi} |P_{ca}^\lambda|^2 \sin\theta_e\, d\theta_e\, d\phi_e . \text{(A-8)}$$

If one defines

$$D_a = \frac{e^2}{2\pi}\sum_\lambda \int_0^\pi\int_0^{2\pi} |P_{ca}^\lambda|^2 \sin\theta_e\, d\theta_e\, d\phi_e \qquad \text{(A-9)}$$

then the real part of Υ_{ii} can be written as

$$Re(\Upsilon_{ii}(E)) = (E-E_c'+k_r)D_a \qquad \text{(A-10)}$$

This expression shows a linear E dependence.

The matrix element P_{ca}^{λ} can be written (10) as

$$P_{ca}^{\lambda} = i\,(E_c - E_a)\,\langle c|\vec{r}\,|a\rangle \cdot \hat{e}_{\lambda} \tag{A-11}$$

where E_a and E_c are the energies of the atomic states $|a\rangle$ and $|c\rangle$, respectively.

Combining Eq.(A-9) and Eq.(A-11), one obtains

$$\begin{aligned} D_a &= \frac{e^2}{2\pi}\,(E_c - E_a)^2 \sum_{\lambda} \int_0^{\pi}\int_0^{2\pi} |\langle c|\vec{r}\,|a\rangle \cdot \hat{e}_{\lambda}|^2 \sin\theta_e\, d\theta_e\, d\phi_e \\ &\simeq e^2\,(E_c - E_a)^2\, a_o^2 \end{aligned} \tag{A-12}$$

where a_o is the Bohr radius and $\sum_{\lambda} \int_0^{\pi}\int_0^{2\pi} |\langle c|\vec{r}\,|a\rangle \cdot \hat{e}_{\lambda}|^2 \sin\theta_e\, d\theta_e\, d\phi_e$ is assumed to be of the order of a_o. For an atomic system, this is a legitimate assumption.

In relativistic units ($\hbar = m = c = 1$), the fine structure constant α is 1/137, the Bohr radius is

$$a_o = e^{-2} = 137$$

and the energy unit in wave numbers is

$$1\ cm^{-1} = 2.24 \times 10^{-10}\ .$$

Thus the energy difference $(E_c - E_a)$ for an atomic system is of the order of 10^{-6} relativistic units and therefore

$$D_a \sim 10^{-10}\ . \tag{A-13}$$

The real part of $\gamma_{jj'}$ can be obtained in a similar fashion:

$$Re(\Upsilon_{jj}(E)) = (E - E_c' + k_\sigma) D_b$$

where D_b is defined by

$$D_b = \frac{e^2}{2\pi} \sum_\lambda \int_0^\pi \int_0^{2\pi} |\langle c| \vec{p} \cdot \hat{e}_\lambda |b\rangle|^2 \sin\theta_e \, d\theta_e \, d\phi_e \ . \qquad \text{(A-14)}$$

The magnitude of D_b is of the same order as that of D_a.

The imaginary parts of $\Upsilon_{ii}(E)$ and $\Upsilon_{jj}(E)$ are

$$Im(\Upsilon_{ii}(E)) = 2 \sum_f \mathcal{P} \left(\frac{H_{fi} H_{if}}{E - E_f'} \right)$$

and

$$Im(\Upsilon_{jj}(E)) = 2 \sum_f \mathcal{P} \left(\frac{H_{fj} H_{jf}}{E - E_f'} \right)$$

where the summation over f is over frequency, direction and polarization of the emitted radiation and $\mathcal{P}$ is the principal value operator defined in Chapter II.

For a continuous distribution of frequencies, the summation over f is replaced by an integral of the form given in Eq.(A-7). Thus one gets

$$Im(\Upsilon_{ii}(E)) = \frac{2L^3}{(2\pi)^3} \sum_\lambda \int_0^\infty \int_0^\pi \int_0^{2\pi} k_\lambda^2 \, dk_\lambda \ \mathcal{P} \left(\frac{|H_{fi}|^2}{E - E_f'} \right) \sin\theta_e \, d\theta_e \, d\phi_e$$

(A-15)

and

$$Im(\Upsilon_{jj}(E)) = \frac{2L^3}{(2\pi)^3} \sum_{\lambda} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} k_\lambda^2 dk_\lambda \, \mathcal{P}\left(\frac{|H_{fj}|^2}{E-E_f'}\right) \sin\theta_e d\theta_e d\phi_e \, .$$

Combining Eq.(2-18), Eq.(A-2) and Eq.(A-15), the imaginary part of $\Upsilon_{ii}(E)$ is written as

$$Im(\Upsilon_{ii}(E)) = \frac{2 \cdot e^2}{(2\pi)^2} \sum_{\lambda} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} k_\lambda dk_\lambda \, \mathcal{P}\left(\frac{1}{E-E_c'+k_\sigma-k_\lambda}\right) |k_{ca}^{\lambda}|^2 \sin\theta_e d\theta_e d\phi_e$$

$$= \frac{e^2}{2\pi^2} \sum_{\lambda} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} k dk \, \mathcal{P}\left(\frac{1}{k_\sigma+E-E_c'-k}\right) \cdot |k_{ca}^{\lambda}|^2 \sin\theta_e d\theta_e d\phi_e \, .$$

The integral

$$\int_0^{\infty} dk \, k \, \mathcal{P}\left(\frac{1}{-k+k_\sigma+E-E_c'}\right)$$

in the previous equation is divergent which means that the imaginary part of $\Upsilon_{ii}(E)$ is infinite. Similarly, it can be shown that the imaginary part of $\Upsilon_{jj}(E)$ is infinite. These imaginary parts $\{Im(\Upsilon_{ii}(E))$ and $Im(\Upsilon_{jj}(E))\}$ are added to the energies, E_a and E_b of the unperturbed atomic states, respectively. This results in a shift of the atomic levels. There is a similar kind of shift in the ground state, contributed by the imaginary part of $\Gamma(E)$. Thus all the atomic states are shifted relative to each other.

It is important to note here that only the relative separartion of the states are required in the discussion. Therefore one can use the method of renormalization of the atomic states by absorbing these infinities in the atomic states ( ). One can then set

$$E_a + \mathrm{Im}\,(\gamma_{ii}) \longrightarrow E_a \quad ,$$

$$E_b + \mathrm{Im}\,(\gamma_{jj}) \longrightarrow E_b \quad ,$$

and

$$E_c + \mathrm{Im}\,(\Gamma) \longrightarrow E_c \quad .$$

3. Evaluation of Γ

The expression for $\Gamma(E)$, obtained from Eq.(2-36) and Eq.(A-3), is

$$-\tfrac{i}{2}\Gamma(E) = e^2\left(\frac{2\pi}{L^3}\right)\sum_{k_r}\frac{n(k_r)}{k_r}\Big[V_{ab}\,p^{\sigma}_{ca}\,p^{\sigma}_{bc} + V_{ba}\,p^{\sigma}_{ac}\,p^{\sigma}_{cb}$$

$$+ |p^{\sigma}_{ca}|^2\{E - E_j' + i/2\,\gamma_{jj}(E)\} + |p^{\sigma}_{cb}|^2\{E - E_i' + i/2\,\gamma_{ii}(E)\}\Big]$$

$$\times\Big[(E - E_i' + i\,\gamma_{ii}(E)/2)(E - E_j' + i\,\gamma_{jj}(E)/2) - |V_{ab}|^2\Big]^{-1}, \qquad \text{(A-16)}$$

For a continuous distribution of absorbed frequencies, the summation over k_σ is replaced by an integration:

$$\sum_{k_\sigma} \longrightarrow \left(\frac{L}{2\pi}\right)^3 \sum_{\sigma} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \rho(k_r)\,dk_r\,\sin\theta_a\,d\theta_a\,d\phi_a$$

where $\rho(k_r)$ represents the density of radiation oscillators in the incident beam with energy between k_r and $k_r + dk_r$. The sum over α is over polarization. The angles θ_a and ϕ_a are the polar and azimuthal angles, respectively, of the wave vector $\vec{k}_\alpha$.

The density $\rho(k_\alpha)$ is written in terms of $I_0(k_\alpha)$, the intensity (energy per unit area) per unit frequency per unit solid angle as

$$\rho(k_\alpha) = \frac{I_0(k_\alpha)}{k_\alpha n(k_\alpha)}$$

where $n(k_\alpha)$ is an average photon occupation number at the frequency k_α of the incident radiation (8). Thus Eq.(A-16) can be written as

$$-i\Gamma(E)/2 = e^2/(2\pi)^2 \sum_\alpha \int_0^\infty dk_\alpha \sin\theta_a d\theta_a d\phi_a \frac{I_0(k_\alpha)}{k_\alpha^2} \Big[V_{ab} p_{ca}^\alpha p_{bc}^\alpha$$

$$+ p_{cb}^\alpha \cdot p_{ac}^\alpha V_{ba} + |p_{ca}^\alpha|^2 \{ E - E_j' + i\gamma_{jj}(E)/2 \}$$

$$+ |p_{cb}^\alpha|^2 \{ E - E_i' + i\gamma_{ii}(E)/2 \} \Big] \times$$

$$\Big[(E - E_i' + i\gamma_{ii}(E)/2)(E - E_j' + i\gamma_{jj}(E)/2)$$

$$- |V_{ab}|^2 \Big]^{-1} \qquad \text{(A-17)}$$

As discussed in the previous section, the imaginary parts of $\gamma_{ii}(E)$ and $\gamma_{jj}(E)$ in Eq.(A-16) are absorbed in the energies E_i and E_j, respectively. The real parts have the following E dependence (see Appendix A-2):

$$Re(\gamma_{ii}(E)) = (E - E_c' + k_\alpha) D_a$$

and

$$Re\,(\Upsilon_{jj}(E)) = (E - E_c' + k_\sigma)D_b \,.$$

Thus, the denominator of $\Gamma(E)$ reduces to

$$\{E - E_a' + k_\sigma + i(E - E_c' + k_\sigma)D_a/2\}\{E - E_b' + k_\sigma + i(E - E_c' + k_\sigma)D_b/2\} - |V_{ab}|^2 .$$

By regrouping the terms and factoring out $(1+iD_a/2).(1+iD_b/2)$, the above expression becomes

$$(1 + iD_a/2)(1 + iD_b/2)\left[\{E - E_a'/(1+iD_a/2) + k_\sigma - iE_c'D_a/(2+iD_a)\}\right.$$

$$\times\{E - E_b'/(1+iD_b/2) + k_\sigma - iE_c'D_b/(2+iD_b)\} - |V_{ab}|^2/\{(1+iD_a/2)$$

$$\left.\times(1+iD_b/2)\}\right] = (1+iD_a/2)(1+iD_b/2)\left[\{E - E_a'/(1+D_a^2/4)\right.$$

$$+ k_\sigma + i(E_a' - E_c')D_a/(2 + D_a^2/2) - E_c'D_a^2/\{4(1+D_a^2/4)\}\}\times$$

$$\left\{E - \frac{E_b'}{1+D_b^2/4} + k_\sigma + \frac{i}{2}\,\frac{E_b' - E_c'}{1+D_b^2/4}\,D_b\right.$$

$$\left. - \frac{E_c'D_b^2}{4(1+D_b^2/4)}\right\} - \frac{|V_{ab}|^2}{(1+D_a^2/4)(1+D_b^2/4)}$$

$$\left. + \frac{|V_{ab}|^2\{D_aD_b/4 + i(D_a + D_b)/2\}}{(1+D_a^2/4)(1+D_b^2/4)}\right]. \qquad \text{(A-18)}$$

Since, the magnitudes of D_a and D_b are very small (see Appendix A-2) compared to unity, the terms $D_a^2/4$, $D_b^2/4$ and $D_aD_b/4$ can be neglected in Eq.(A-18). Thus the denominator reduces to

$$(1+iD_a/2)(1+iD_b/2)[\{k_\sigma - E_a' + E - E_c' D_a^2/4$$

$$+ i(E_a' - E_c')D_a/2\} \times \{k_\sigma - E_b' + E - E_c' D_b^2/4 + i(E_b' - E_c')D_b/2\}$$

$$-|V_{ab}|^2\{1 - i(D_a + D_b)/2\} = (1+iD_a/2)(1+iD_b/2)[\{k_\sigma - E_a''$$

$$+ i\gamma_a/2\} \times \{k_\sigma - E_b'' + i\gamma_b/2\} - |V_{ab}|^2\{1 - i(D_a+D_b)/2\}] \qquad \text{(A-19)}$$

where

$$E_a'' = E_a' + \frac{E_c' D_a^2}{4} - E \; ,$$
$$E_b'' = E_b' + \frac{E_c' D_b^2}{4} - E \; , \qquad \text{(A-20)}$$

and γ_a and γ_b are defined in Eq.(2-43).

In Eq.(A-20), the terms $E_c' D_a^2/4$ and $E_c' D_b^2/4$ are very small compared to other terms and therefore they can be neglected. Thus one gets

$$E_a'' = E_a' - E$$

and

$$E_b'' = E_b' - E$$

The expression in Eq.(A-19) can be written as

$$(1+iD_a/2)(1+iD_b/2)(k_\sigma - k_1)(k_\sigma - k_2) \qquad \text{(A-21)}$$

where k_1 and k_2 are the two roots of the quadratic equation

$$(k_\sigma - E_a'' + i\gamma_a/2)(k_\sigma - E_b'' + i\gamma_b/2) - |V_{ab}|^2\{1 - i(D_a+D_b)/2\} = 0.$$

The roots are

$$\left.\begin{matrix} k_1 \\ k_2 \end{matrix}\right\} = (E_a' + E_b')/2 - E - i(\gamma_a + \gamma_b)/4 \pm \tfrac{1}{2}\left[\Delta^2 - x^2 + 4|V_{ab}|^2 - i\,2\{\Delta x + |V_{ab}|^2 (D_a + D_b)\}\right]^{1/2} \tag{A-22}$$

where

$$\Delta = E_a' - E_b'$$

and (A-23)

$$x = (\gamma_a - \gamma_b)/2 \ .$$

The complex quantity inside the square root sign in Eq.(A-22) can be separated into real and imaginary parts as follows:

If

$$Y = [A + iB]^{\frac{1}{2}}$$

then

$$Re(Y) = \frac{1}{\sqrt{2}}\left[(A^2+B^2)^{\frac{1}{2}} + A\right]^{\frac{1}{2}}$$

and (A-24)

$$Im(Y) = \frac{1}{\sqrt{2}}\left[(A^2+B^2)^{\frac{1}{2}} - A\right]^{\frac{1}{2}}.$$

Thus one gets

$$\left.\begin{matrix} k_1 \\ k_2 \end{matrix}\right\} = (E_a' + E_b')/2 - E \pm R - i(x_3 \pm I)$$

where

$$\left.\begin{matrix} R \\ I \end{matrix}\right\} = \frac{1}{2\sqrt{2}}\left[\left\{(\Delta^2 - x^2 + 4|V_{ab}|^2)^2 + 4\{x\Delta + |V_{ab}|^2 (D_a + D_b)\}^2\right\}^{\frac{1}{2}} \pm (\Delta^2 - x^2 + 4|V_{ab}|^2)\right]^{\frac{1}{2}} \tag{A-25}$$

and

$$x_3 = \frac{\gamma_a + \gamma_b}{4} \ . \tag{A-26}$$

Since D_a and D_b are much less than one, the term $4|V_{ab}|^2(D_a+D_b)^2$ in the expression for R and I, can be neglected compared to the other terms. Thus one obtains

$$\left.\begin{matrix} R \\ I \end{matrix}\right\} = \frac{1}{2\sqrt{2}} \Big[\{ (\Delta^2 - X^2 + 4V^2)^2 + 4\Delta^2 X^2 \}^{1/2} \pm (\Delta^2 - X^2 + 4V^2) \Big]^{1/2} \tag{A-27}$$

where

$$V^2 = |V_{ab}|^2$$

Thus, substituting the real parts of γ_{ii} and γ_{jj} from Appendix A-2 into Eq.(A-17), combining Eq.(A-17) and Eq.(A-21) and rearranging, one gets

$$-i\Gamma(E)/2 = \frac{e^2}{(2\pi)^2} \sum_\sigma \int_0^\infty \int_0^\pi \int_0^{2\pi} dk_\sigma \sin\theta_a d\theta_a d\phi_a \frac{I_0(k_\sigma)}{k_\sigma^2} \Big[\{ V_{ab} p^\sigma_{ca} p^\sigma_{bc} + V_{ab} p^\sigma_{cb} p^\sigma_{ac} + |p^\sigma_{ca}|^2 \{ k_\sigma(1 + iD_a/2) - E'_b + E(1+iD_b/2) - \tfrac{i}{2} E'_c D_b \} + |p^\sigma_{cb}|^2 \{ k_\sigma (1 + iD_b/2) - E'_a + E(1+iD_a/2) - iE'_c D_a/2 \} \} \times \{ (1+iD_a/2)(1+iD_b/2)(k_\sigma - k_1)(k_\sigma - k_2) \}^{-1} \Big] \tag{A-28}$$

If the incident beam is monochromatic then the intensity $I_0(k_\sigma)$ in Eq.(A-28) is replaced by $\bar{I}_0 \delta(k_\sigma - k_\sigma^0)$, where $\bar{I}_0$ is a constant, which determines the intensity of the incident beam and $\delta(k_\sigma - k_\sigma^0)$ is a Dirac delta function. The frequency k_σ^0 is the frequency of the incident beam. Thus, for this case, Eq.(A-28) reduces to:

$$-\frac{i}{2}\Gamma(E) = \frac{e^2}{(2\pi)^2}\sum_{\alpha}\int_0^{\pi}\int_0^{2\pi}\sin\theta_a d\theta_a d\phi_a \frac{\bar{I}_o}{k_\alpha^{o2}}\Big[V_{ab} p_{ca}^{\alpha} p_{bc}^{\alpha}$$

$$+ V_{ba} p_{ac}^{\alpha} p_{cb}^{\alpha} + |p_{ca}^{\alpha}|^2\{ k_\alpha^o(1+iD_b/2) - E_b' + E(1+iD_b/2) - iE_c' D_b/2\}$$

$$+ |p_{cb}^{\alpha}|^2\{ k_\alpha^o(1+iD_a/2) - E_a' + (1+iD_a/2)E - iE_c' D_a/2\}\Big]$$

$$\times\left[(1+iD_a/2)(1+iD_b/2)(k_\alpha^o - k_1)(k_\alpha^o - k_2)\right]^{-1} \quad \text{(A-29)}$$

when the state $|b\rangle$ is non-decaying ($\gamma_b = 0$), then Eq.(A-29) becomes

$$-\frac{i}{2}\Gamma(E) = \frac{D_a \bar{I}_o}{k_\alpha^{o2}}\cdot\frac{k_\alpha^o - E_b'/(1+iD_b/2) + E - iE_c' D_b/(2+iD_b)}{(1+iD_a/2)(k_\alpha^o - k_1)(k_\alpha^o - k_2)} \quad \text{(A-30)}$$

where D_a and D_b are defined in Eq.(A-9) and Eq.(A-14).

Multiplying the numerator and denominator of Eq.(A-30) by $(1-iD_a/2)$, neglecting the term $D_a^2/4$ compared to unity and rearranging the denominator one gets,

$$-\frac{i}{2}\Gamma(E) = \frac{D_a\bar{I}_o\,(k_\alpha^o - E_b' + E + i(E_b' - E_c')D_b/2)(1-iD_a/2)}{k_\alpha^{o2}\left[k_\alpha^o - (E_a' + E_b')/2 + E - R + i(X_3 + I)\right]}$$

$$\times\left[k_\alpha^o - (E_a' + E_b')/2 + E + R + i(X_3 - I)\right]^{-1} \quad \text{(A-31)}$$

where R, I and X_3 are defined in Eq.(A-25) and Eq.(A-26).

For an incident monochromatic line of power 10^{-3} watts, the factor $D_a I_o/k_\alpha^{o2}$ is of the order of $10^{-4}E_c'$ ($D_a \sim 10^{-10}$; $I_o \sim 10^{-11}$ and

$E_c' \sim 10^{-5}$ in relativistic units). Thus, the magnitude of $\Gamma(E)$ is very small compared to E_c'. Therefore one finds that the pole of G(E) obtained from equation:

$$E - E_c' + \frac{i}{2}\Gamma(E) = 0 \tag{A-33}$$

is not significantally different from the pole

$$E = E_c' - \frac{i}{2}\Gamma(E_c') \tag{A-33}$$

where $\Gamma(E)$ is evaluated at $E = E_c'$.

The expression for $\Gamma(E_c')$ is:

$$-\frac{i}{2}\Gamma(E_c') = \frac{D_a \bar{I}_o}{k_\sigma^{o\,2}} \frac{(k_\sigma^o - E_b' + E_c' + i(E_b' - E_c')D_b/2)(1 - iD_a/2)}{[k_\sigma^o - (E_a' + E_b')/2 + E_c' - R + i(X_3 + I)]}$$

$$\times [k_\sigma^o - (E_a' + E_b')/2 + E_c' + R + i(X_3 - I)]^{-1} \tag{A-34}$$

The real part of $\Gamma(E_c')$ gives the decay constant of the ground state $|c\rangle$ (see Eq.(2-54)) and the imaginary part is absorbed in the energy E_c of the ground state, giving rise to an energy shift. In this case, the decay constant $Re(\Gamma)$ depends on the frequency of the incident beam.

If the incident beam is such that the energy per unit area per unit solid angle per unit frequency, I_o is constant (white light beam) then Eq.(A-28) reduces to

$$-\frac{i}{2}\Gamma(E) = \frac{e^2}{(2\pi)^2} I_o \sum_\sigma \int_0^\infty \int_0^\pi \int_0^{2\pi} dk_\sigma \sin\theta_a d\theta_a d\phi_a \frac{1}{k_\sigma^2}\Big[\{V_{ab} P_{ca}^\sigma P_{bc}^\sigma$$

$$+ V_{ba} P_{ac}^\sigma P_{cb}^\sigma + |P_{ca}^\sigma|^2 \{k_\sigma(1 + iD_b/2) - E_b' + E(1 + iD_b/2) - iE_c' D_b/2\}$$

$$+ |P_{cb}^\sigma|^2 \{k_\sigma(1 + iD_a/2) - E_a' + E(1 + iD_a/2) - iE_c' D_a/2\}\Big]$$

$$\times (1 + iD_a/2)(1 + iD_b/2)(k_\sigma - k_1)(k_\sigma - k_2). \qquad \text{(A-35)}$$

The term in the square bracket in Eq.(A-35) is a highly peaked function near the real parts of the poles. Thus one can replace $1/k_\sigma^2$ in Eq.(A-35) by an average value $1/k_0^2$. Thus one gets

$$-\frac{i}{2}\Gamma(E) = \frac{e^2}{(2\pi)^2} \cdot \frac{I_0}{k_0^2} \sum_\sigma \int_0^\pi \int_0^{2\pi} \frac{\sin\theta_a \, d\theta_a \, d\phi_a}{(1 + iD_a/2)(1 + iD_b/2)} \Big[\{ V_{ab} p_{ca}^\sigma p_{bc}^\sigma$$

$$+ V_{ba} p_{ac}^\sigma p_{cb}^\sigma + |p_{ca}^\sigma|^2 (E(1 + iD_b/2) - E_b' - iE_c' D_b/2)$$

$$+ |p_{cb}^\sigma|^2 (E(1 + iD_a/2) - E_a' - iE_c' D_a/2) \} I_1$$

$$+ \{ |p_{ca}^\sigma|^2 (1 + iD_b/2) + |p_{cb}^\sigma|^2 (1 + iD_a/2) \} I_2 \Big] \qquad \text{(A-36)}$$

where

$$I_1 = \int_0^\infty \frac{dk}{(k-k_1)(k-k_2)}$$

and

$$I_2 = \int_0^\infty \frac{k\,dk}{(k-k_1)(k-k_2)} .$$

The limits in the integrals of I_1 and I_2 can be extended into the non-physical region ($k = -\infty$ to $k = 0$) without significant error, because the integrands are negligible in this region. Thus one gets

$$I_1 = \int_{-\infty}^\infty \frac{dk}{(k-k_1)(k-k_2)} \qquad \text{(A-37)}$$

and

$$I_2 = \int_{-\infty}^\infty dk \; k / \{ (k-k_1)(k-k_2) \}$$

The method of contour integration is used to evaluate I_1 and I_2. The results are:

$$I_1 = 0$$
$$I_2 = -i\pi \tag{A-38}$$

Thus, from Eq.(A-36) and Eq.(A-38) one obtains

$$Re(\Gamma(E)) = \frac{e^2}{(2\pi)^3} \cdot \frac{I_0}{k_0^2} \sum_{\sigma} \int_0^{\pi}\int_0^{2\pi} \sin\theta_a \, d\theta_a \, d\phi_a \{ |P_{ca}^{\sigma}|^2 + |P_{cb}^{\sigma}|^2 \}. \tag{A-39}$$

In the above equation, the terms $D_a^2/4$, $D_b^2/4$ and $D_aD_b/4$ are neglected compared to unity. This shows that $Re(\Gamma)$ does not depend on E. The average photon occupation number $n(k_0)$, in the incident beam is of the order of I_0/k_0^3. Thus Eq.(A-39) can be written as

$$Re(\Gamma) \sim n(k_0)\, k_0 \frac{e^2}{(2\pi)^2} \sum_{\sigma} \int_0^{\pi}\int_0^{2\pi} \sin\theta_a \, d\theta_a \, d\phi_a \{ |P_{ca}^{\sigma}|^2 + |P_{cb}^{\sigma}|^2 \}$$

$$\sim n(k_0)\, (\gamma_a + \gamma_b) \tag{A-40}$$

where γ_a and γ_b are defined in Eq.(2-43)

$$k_0 \sim (E_a' - E_c') \sim (E_b' - E_c')$$

Equation (A-40) shows that the magnitude of $Re(\Gamma)$ is very small compared to γ_a or γ_b provided the intensity of the incident beam is not too high.

APPENDIX B

1. Evaluation of $P(\hat{e}_\sigma, k_\lambda)$

The probability of emission of a photon with a wave vector $\vec{k}_\lambda$ and polarization $\hat{e}_\lambda$ is

$$P(\hat{e}_\sigma, k_\lambda) = \sum_{k_\sigma} |b_f(\infty)|^2$$

as defined in Eq.(2-59).

For a continuous distribution of frequencies in the incident radiation field, the summation over k_σ is replaced by an integration

$$\sum_{k_\sigma} \longrightarrow \left(\frac{L}{2\pi}\right)^3 \int_0^\infty \rho(k_\sigma)\, dk_\sigma$$

where

$$\rho(k_\sigma) = \frac{I_o(k_\sigma)}{n(k_\sigma)\, k_\sigma} \,.$$

Thus, one can write

$$P(\hat{e}_\sigma, k_\lambda) = \left(\frac{L}{2\pi}\right)^3 \cdot \int_0^\infty \frac{I_o(k_\sigma)}{n(k_\sigma)\, k_\sigma} |b_f(\infty)|^2 dk_\sigma \,. \qquad \text{(B-1)}$$

From Eq.(2-58), one finds that $|b_f(\infty)|^2$ contains a factor $1/|(E_f' - E_3)|^2$ which reduces to a Dirac delta function in the limit when $\Gamma \to 0$. This can be seen as follows:

$$|(E_f' - E_3')|^{-2} = \left[(k_\lambda - k_\sigma)^2 + \Gamma^2/4\right]^{-1}$$

$$= \frac{2\pi}{\Gamma}\, \delta(k_\lambda - k_\sigma) \qquad \text{(B-2)}$$

where Γ stands for the real part of Γ and the imaginary part is absorbed in the atomic state E_c. In Eq.(B-2), the following representation of the Dirac delta function is used

$$\delta(x) = \frac{1}{\pi} \lim_{\sigma \to 0} \frac{\sigma}{x^2 + \sigma^2}$$

The assumption that Γ is very small is appropriate provided the intensity of the incident beam is not too high ($n(k_\sigma) \ll 1$) (see Eq.(A-40)).

From Eq.(2-51), Eq.(2-58), Eq.(A-3) and Eq.(A-5), $b_f(t\to\infty)$ is written as

$$b_f(t\to\infty) = \frac{2\pi e^2 \sqrt{n(k_\sigma)}}{L^3 \sqrt{k_\sigma k_\lambda}} \Big[V_{ab} P^\lambda_{ca} P^\sigma_{bc} + V_{ba} P^\lambda_{cb} P^\sigma_{ac}$$

$$+ P^\lambda_{ca} P^\sigma_{ac} (k_\lambda - E'_b + E'_c + i\gamma_b/2) + P^\lambda_{cb} P^\sigma_{bc} (k_\lambda - E'_a + E'_c + i\gamma_a/2) \Big]$$

$$\times \Big[\{ (k_\lambda - k_\sigma) + i\Gamma/2 \} (k_\lambda - k'_1)(k_\lambda - k'_2) \Big]^{-1} e^{-iV_{cc}t}$$

where

$$\left. \begin{matrix} k'_1 \\ k'_2 \end{matrix} \right\} = (E'_a + E'_b)/2 - E'_c \pm R - i(X_3 \pm I) , \qquad \text{(B-3)}$$

and R, I and X_3 are defined in Eq.(A-25) and Eq.(A-26).

Thus, the probability of having a photon with wave vector $\vec{k}_\lambda$ emitted, provided a photon with wave vector $\vec{k}_\sigma$ was absorbed is

$$|b_f(\infty)|^2 = \frac{2\pi^2 e^4 \, n(k_\sigma)}{L^6 \, k_\sigma k_\lambda} \cdot \frac{1}{(k_\lambda - k_\sigma)^2 + \Gamma^2/4} \cdot \frac{N_1}{D_1} \qquad \text{(B-4)}$$

$$
\begin{aligned}
N_1 = {} & |p^{\lambda}_{ca}|^2 |p^{\sigma}_{ac}|^2 [(k_\lambda - E_b' + E_c')^2 + \gamma_b^2/4] \\
& + |p^{\lambda}_{cb}|^2 |p^{\sigma}_{bc}|^2 [(k_\lambda - E_a' + E_c')^2 + \gamma_a^2/4] \\
& + V^2 \{ |p^{\lambda}_{ca}|^2 |p^{\sigma}_{bc}|^2 + |p^{\lambda}_{cb}|^2 |p^{\sigma}_{ac}|^2 + 2\,\mathrm{Re}(p^{\lambda}_{ca} p^{\sigma}_{bc} p^{\lambda *}_{cb} p^{\sigma *}_{ac}) \} \\
& + 2V [(k_\lambda - E_b' + E_c') \{ |p^{\lambda}_{ca}|^2 \mathrm{Re}(p^{\sigma}_{bc} p^{\sigma *}_{ac}) + |p^{\sigma}_{ac}|^2 \mathrm{Re}(p^{\lambda}_{cb} p^{\lambda *}_{ca}) \} \\
& + (k_\lambda - E_a' + E_c') \{ |p^{\lambda}_{cb}|^2 \mathrm{Re}(p^{\sigma}_{ac} p^{\sigma *}_{bc}) + |p^{\sigma}_{bc}|^2 \mathrm{Re}(p^{\lambda}_{ca} p^{\lambda *}_{cb}) \} \\
& + (\gamma_a |p^{\lambda}_{cb}|^2 - \gamma_b |p^{\lambda}_{ca}|^2) \tfrac{1}{2} \mathrm{Im}(p^{\sigma}_{ac} p^{\sigma *}_{bc}) + (\gamma_a |p^{\sigma}_{bc}|^2 - \gamma_b |p^{\sigma}_{ac}|^2) \tfrac{1}{2} \mathrm{Im}(p^{\lambda}_{ca} p^{\lambda *}_{cb})] \\
& + [(k_\lambda - E_a' + E_c')(k_\lambda - E_b' + E_c') + \gamma_a \gamma_b / 4] .\, 2 .\, \mathrm{Re}(p^{\lambda}_{ca} p^{\lambda *}_{cb} p^{\sigma}_{ac} p^{\sigma *}_{bc}) \\
& + [\gamma_a (k_\lambda - E_b' + E_c') - \gamma_b (k_\lambda - E_a' + E_c')]\, \mathrm{Im}(p^{\lambda}_{ca} p^{\lambda *}_{cb} p^{\sigma}_{ac} p^{\sigma *}_{bc})
\end{aligned}
$$

and

$$
\begin{aligned}
D_1 = {} & \{ (k_\lambda - E_a' + E_c')^2 + \gamma_a^2/4 \} \{ (k_\lambda - E_b + E_c')^2 + \gamma_b^2/4 \} + V^4 \\
& - 2V^2 \{ (k_\lambda - E_a' + E_c')(k_\lambda - E_b' + E_c') - \gamma_a \gamma_b / 4 \}
\end{aligned}
$$

Thus, combining Eq.(B-1), Eq.(B-2) and Eq.(B-4), one gets

$$
P(\hat{e}_\sigma, k_\lambda) = \frac{e^4}{L^3 \Gamma k_\lambda} \cdot \left(\frac{I_0(k_r)}{k_r^2} \right)_{k_r = k_\lambda} \cdot \frac{N_1}{D_1} \quad .
$$

For an incident radiation beam with constant intensity I_0 (white light), the probability of having a photon with wave vector $\vec{k}_\lambda$ is

$$P(\hat{e}_\sigma, k_\lambda) = \frac{e^4 I_0 N_1}{L^3 \Gamma k_\lambda^3 D_1} \tag{B-5}$$

This probability $P(\hat{e}_\sigma, k_\lambda)$ depends on the direction and polarization of the incident radiation through the matrix elements p_{ac}^{σ} and p_{bc}^{σ}.

It is shown in Chapter III that $P(\hat{e}_\sigma, k_\lambda)$ is a highly peaked function near k_λ equal to the frequency difference between the perturbed excited states and the ground state. Thus one can replace $1/k_\lambda^3$ by an average value $1/k_0{}^3$. Therefore $P(\hat{e}_\sigma, k_\lambda)$ reduces to

$$P(\hat{e}_\sigma, k_\lambda) = \frac{e^4 I_0 N_1}{L^3 \Gamma k_0^3 D_1} \tag{B-6}$$

In terms of a new variable

$$K = k_\lambda - (E_a' + E_b')/2 + E_c' \tag{B-7}$$

one can write

$$N_1 = \{(K+\Delta/2)^2 + \gamma_b^2/4\}|p_{ca}^{\lambda}|^2|p_{ac}^{\sigma}|^2 + \{(K-\Delta/2)^2 + \gamma_a^2/4\}|p_{cb}^{\lambda}|^2|p_{bc}^{\sigma}|^2$$

$$+ V^2\{|p_{ca}^{\lambda}|^2|p_{bc}^{\sigma}|^2 + |p_{cb}^{\lambda}|^2|p_{ac}^{\sigma}|^2 + 4\,\mathrm{Re}(p_{ca}^{\lambda}p_{cb}^{\lambda *})\,\mathrm{Re}(p_{ac}^{\sigma}p_{bc}^{\sigma *})$$

$$- 2\,\mathrm{Re}(p_{ca}^{\lambda}p_{cb}^{\lambda *}p_{ac}^{\sigma}p_{bc}^{\sigma *})\}$$

$$+ 2V[\{(K+\Delta/2)|p_{ca}^{\lambda}|^2 + (K-\Delta/2)|p_{cb}^{\lambda}|^2\}\,\mathrm{Re}(p_{ac}^{\sigma}p_{bc}^{\sigma *})$$

$$\{ (K+\Delta/2)|P_{ac}^{\sigma}|^2 + (K-\Delta/2)|P_{bc}^{\sigma}|^2 \} \, \mathrm{Re}\,(P_{ca}^{\lambda} P_{cb}^{\lambda *})$$

$$+ (\gamma_a |P_{cb}^{\lambda}|^2 - \gamma_b |P_{ca}^{\lambda}|^2) \tfrac{1}{2} \,\mathrm{Im}\,(P_{ac}^{\sigma} P_{bc}^{\sigma *})$$

$$+ (\gamma_a |P_{bc}^{\sigma}|^2 - \gamma_b |P_{ac}^{\sigma}|^2) \tfrac{1}{2} \,\mathrm{Im}\,(P_{ca}^{\lambda} P_{cb}^{\lambda *})$$

$$+ \{ (K-\Delta/2)(K+\Delta/2) + \gamma_a \gamma_b /4 \} \, 2 . \mathrm{Re}\,(P_{ca}^{\lambda} P_{cb}^{\lambda *} P_{ac}^{\sigma} P_{bc}^{\sigma *})$$

$$\{ \gamma_a (K+\Delta/2) - \gamma_b (K-\Delta/2) \} \times$$

$$\mathrm{Im}\,(P_{ca}^{\lambda} P_{cb}^{\lambda *} P_{ac}^{\sigma} P_{bc}^{\sigma *}) \qquad \text{(B-8)}$$

and

$$D_1 = (K-\Delta/2)^2 (K+\Delta/2)^2 + (K+\Delta/2)^2 \gamma_a^2/4$$

$$+ (K-\Delta/2)^2 \gamma_b^2/4 - 2V^2 (K-\Delta/2)(K+\Delta/2)$$

$$+ (V^2 + \gamma_a \gamma_b /4)^2 \quad . \qquad \text{(B-9)}$$

2. Evaluation of $I(\Omega_a,\Omega_e,\sigma,\lambda)$

The intensity of the scattered radiation with polarization λ and direction (θ_e, ϕ_e), for a given incident radiation with polarization σ and direction (θ_a, ϕ_a), is defined in Eq.(2-61) as

$$I(\Omega_a,\Omega_e,\sigma,\lambda) = \frac{L^3}{(2\pi)^3}\int_0^\infty P(\hat{e}_\sigma,k_\lambda)\,k_\lambda^2\,dk_\lambda \,.$$

Combining Eq.(B-5) with the above equation, one obtains

$$I(\Omega_a,\Omega_e,\sigma,\lambda) = \frac{e^4 I_0}{(2\pi)^3\Gamma}\int_0^\infty \frac{N_1}{k_\lambda D_1}\,dk_\lambda \,. \qquad \text{(B-10)}$$

Since N_1/D_1 is a highly peaked function near the real parts of the poles of N_1/D_1, one can replace $1/k_\lambda$ by an average value $1/k_0$ near the poles. Therefore one can write

$$I(\Omega_a,\Omega_e,\sigma,\lambda) = \frac{e^4 I_0}{(2\pi)^3\Gamma k_0}\int_0^\infty \frac{N_1}{D_1}\,dk_\lambda \,. \qquad \text{(B-11)}$$

The limit in this integral can be extended into non-physical region ($k_\lambda = -\infty$ to $k_\lambda = 0$) without significant error, because the integrand is negligible in this region. Thus Eq.(B-11) reduces to

$$I(\Omega_a,\Omega_e,\sigma,\lambda) = \frac{e^4 I_0}{(2\pi)^3\Gamma k_0}\int_{-\infty}^\infty \frac{N_1}{D_1}\,dk_\lambda \qquad \text{(B-12)}$$

The numerator N_1 of the integrand can be written as

$$N_1 = N_0' + N_1' k_\lambda + N_2' k_\lambda^2 \tag{B-13}$$

where

$$\begin{aligned}
N_0' = {} & \{(E_b' - E_c')^2 + \gamma_b^2/4\} |p_{ca}^{\lambda}|^2 |p_{ac}^{\sigma}|^2 + \{(E_a' - E_c')^2 + \gamma_a^2/4\} |p_{cb}^{\lambda}|^2 |p_{bc}^{\sigma}|^2 \\
& + V^2 \{ |p_{ca}^{\lambda}|^2 |p_{bc}^{\sigma}|^2 + |p_{cb}^{\lambda}|^2 |p_{ac}^{\sigma}|^2 + 4\,\mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *})\,\mathrm{Re}(p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& \qquad - 2\,\mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) \} \\
& - 2V [\{ (E_b' - E_c') |p_{ca}^{\lambda}|^2 + (E_a' - E_c') |p_{cb}^{\lambda}|^2 \} \mathrm{Re}(p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& + \{ (E_b' - E_c') |p_{ac}^{\sigma}|^2 + (E_a' - E_c') |p_{bc}^{\sigma}|^2 \} \mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *}) \\
& \quad + \tfrac{1}{2} (\gamma_a |p_{cb}^{\lambda}|^2 - \gamma_b |p_{ca}^{\lambda}|^2) \,\mathrm{Im}(p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& \quad + \tfrac{1}{2} (\gamma_a |p_{bc}^{\sigma}|^2 - \gamma_b |p_{ac}^{\sigma}|^2) \,\mathrm{Im}(p_{ca}^{\lambda} p_{cb}^{\lambda *})] \\
& + \{ (E_a' - E_c')(E_b' - E_c') + \gamma_b \gamma_a / 4 \} \, 2\,\mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& + \{ \gamma_b (E_a' - E_c') - \gamma_b (E_b' - E_c') \} \,\mathrm{Im}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) ,
\end{aligned} \tag{B-14}$$

$$\begin{aligned}
N_1' = {} & -2 \{ (E_b' - E_c') |p_{ca}^{\lambda}|^2 |p_{ac}^{\sigma}|^2 + (E_a' - E_c') |p_{cb}^{\lambda}|^2 |p_{bc}^{\sigma}|^2 \} \\
& + 2V [\{ |p_{ca}^{\lambda}|^2 + |p_{cb}^{\lambda}|^2 \} \mathrm{Re}(p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& \quad + \{ |p_{ac}^{\sigma}|^2 + |p_{bc}^{\sigma}|^2 \} \mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *}) \\
& - (E_b' + E_a' - 2E_c') \, 2\,\mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) \\
& + (\gamma_a - \gamma_b) \,\mathrm{Im}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) ,
\end{aligned} \tag{B-15}$$

and

$$N_2' = |p_{ca}^{\lambda}|^2 |p_{ac}^{\sigma}|^2 + |p_{cb}^{\lambda}|^2 |p_{bc}^{\sigma}|^2$$

$$+ 2\,\mathrm{Re}(p_{ca}^{\lambda} p_{cb}^{\lambda *} p_{ac}^{\sigma} p_{bc}^{\sigma *}) \qquad \text{(B-16)}$$

and the denominator, one can write

$$D_1 = (k_\lambda - k_1')(k_\lambda - k_2')(k_\lambda - k_1'^*)(k_\lambda - k_2'^*) \qquad \text{(B-17)}$$

where k_1' and k_2' are defined in Eq.(B-3).

Thus the integral in Eq.(B-12) reduces to

$$\int_{-\infty}^{\infty} \frac{N_1}{D_1}\, dk = N_0' I_1' + N_1' I_2' + N_2' I_3' \qquad \text{(B-18)}$$

where

$$I_1' = \int_{-\infty}^{\infty} \frac{dk}{(k - k_1')(k - k_2')(k - k_1'^*)(k - k_2'^*)} \quad ,$$

$$I_2' = \int_{-\infty}^{\infty} \frac{k\, dk}{(k - k_1')(k - k_2')(k - k_1'^*)(k - k_2'^*)} \quad ,$$

and

$$I_3' = \int_{-\infty}^{\infty} \frac{k^2\, dk}{(k - k_1')(k - k_2')(k - k_1'^*)(k - k_2'^*)} \quad .$$

The method of contour integration is used to evaluate these integrals. It can be shown that the integrands vanish on a semicircle of infinite radius on both sides (upper half and lower half) of the complex plane. Thus the contour of integration can be chosen either along C_1 or C_2 (see Fig. B-1).

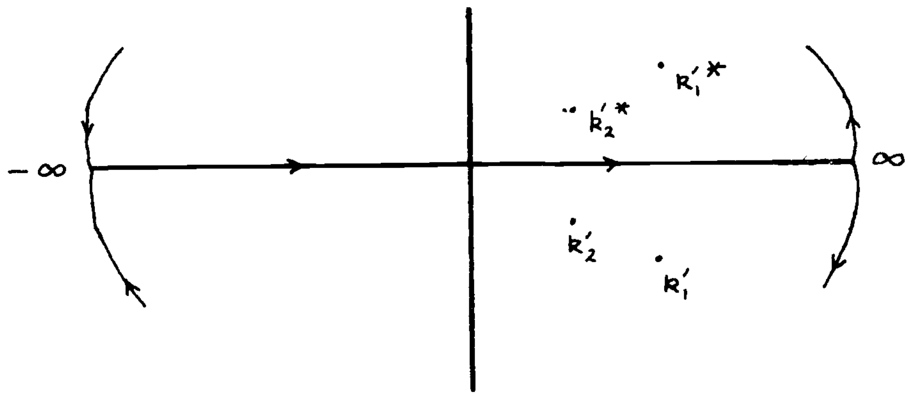

Fig. B-1. Position of the poles in complex plane.

Taking one of the contours, one gets the following results for the integrals:

$$I_1' = \pi \frac{\mathrm{Im}\,(k_1'+k_2')}{\mathrm{Im}\,(k_1')\,\mathrm{Im}(k_2')\,[\,2\,\mathrm{Re}\,(k_1'k_2') - |k_1'|^2 - |k_2'|^2]}\,,$$

$$I_2' = \pi \frac{\mathrm{Im}\,(k_1'k_2')}{\mathrm{Im}(k_1')\,\mathrm{Im}(k_2')\,[\,2\,\mathrm{Re}\,(k_1'k_2') - |k_1'|^2 - |k_2'|^2]}\,,$$

and

$$I_3' = \frac{\pi[|k_1'|^2 \operatorname{Im}(k_2') + |k_2'|^2 \operatorname{Im}(k_1')]}{\operatorname{Im}(k_1')\operatorname{Im}(k_2')[2\operatorname{Re}(k_1' k_2') - |k_1'|^2 - |k_2'|^2]} \ .$$

Substituting the values of k_1' and k_2' (see Eq.(B-3)), the above expressions reduce to:

$$I_1' = 8\pi X_3 / D \ , \tag{B-19}$$

$$I_2' = 8\pi (X_3 E' \pm X\Delta)/D \tag{B-20}$$

and

$$I_3' = 8\pi \frac{E'^2 X_3 + X_3^2 \pm E'\Delta X/2 + (4V^2 + \Delta^2 - X^2) X_3/4}{D} \tag{B-21}$$

where

$$E' = \frac{E_a' + E_b'}{2} - E_c' \ ,$$

and

$$D = 16 X_3^4 - X^2 \Delta^2 + 4 X_3^2 (4V^2 + \Delta^2 - X^2) \ .$$

The definitions of Δ , X, X_3 and V are given in Eq.(A-23), Eq.(A-26) and Eq.(A-27).

Combining Eq.(B-12), Eq.(B-14) to Eq.(B-16) and Eq.(B-18) to Eq.(B-21) one gets the following expression for the intensity of the scattered radiation:

$$I(\Omega_a,\Omega_e,\sigma,\lambda) = \frac{e^4 I_0}{8\pi^2 \Gamma k_0}\Big[\frac{|P_{ca}^{\lambda}|^2 |P_{ac}^{\sigma}|^2}{x_a} + \frac{|P_{cb}^{\lambda}|^2 |P_{bc}^{\sigma}|^2}{x_b}$$

$$+V^2(x_a+x_b)x_a x_b \Big\{ \frac{4\,\mathrm{Re}(P_{ca}^{\lambda} P_{cb}^{\lambda *})\,\mathrm{Re}(P_{ac}^{\sigma} P_{bc}^{\sigma *})}{x_a x_b}$$

$$-\left(|P_{ca}^{\lambda}|^2/x_a - |P_{cb}^{\lambda}|^2/x_b\right)\left(|P_{ac}^{\sigma}|^2/x_a - |P_{bc}^{\sigma}|^2/x_b\right)\Big\}$$

$$+V(x_a+x_b)\Big[\Delta\{(|P_{ca}^{\lambda}|^2 - |P_{cb}^{\lambda}|^2)\,\mathrm{Re}(P_{ac}^{\sigma} P_{bc}^{\sigma *}) + (|P_{ac}^{\sigma}|^2 - |P_{bc}^{\sigma}|^2)\,\mathrm{Re}(P_{ca}^{\lambda} P_{cb}^{\lambda *})\}$$

$$-2\{(|P_{ca}^{\lambda}|^2 x_b - |P_{cb}^{\lambda}|^2 x_a)\,\mathrm{Im}(P_{ac}^{\sigma} P_{bc}^{\sigma *})$$

$$+(|P_{ac}^{\sigma}|^2 x_b - |P_{bc}^{\sigma}|^2 x_a)\,\mathrm{Im}(P_{ca}^{\lambda} P_{cb}^{\lambda *})\}\Big]$$

$$+4x_a x_b\{(x_a+x_b)\,\mathrm{Re}(P_{ca}^{\lambda} P_{cb}^{\lambda *} P_{ac}^{\sigma} P_{bc}^{\sigma *}) + \Delta\,\mathrm{Im}(P_{ca}^{\lambda} P_{ac}^{\sigma} P_{cb}^{\lambda *} P_{bc}^{\sigma *})\}\Big]$$

$$\times\left[(x_a+x_b)^2(V^2+x_a x_b) + \Delta^2 x_a x_b\right]^{-1} \qquad \text{(B-22)}$$

where

$$x_a = \gamma_a/2\ ,$$

and (B-23)

$$x_b = \gamma_b/2\ .$$

APPENDIX C

Eigenvalues and Eigenvector of $\mathcal{H}$

In the Schrödinger representation, the Hamiltonian of the atom with an external perturbation V is

$$\mathcal{H} = H_o + V$$

where H_o is the Hamiltonian of the unperturbed atom.

In order to obtain the eigenvalues and eigenstates of the Hamiltonian $\mathcal{H}$, one has to solve the time-independent Schrodinger equation:

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle \tag{C-1}$$

The state vector $|\Psi\rangle$ can be written in terms of the eigenvectors $|a\rangle$ and $|b\rangle$ of H_o as

$$|\Psi\rangle = C_o|a\rangle + D_o|b\rangle \tag{C-2}$$

where C_o and D_o are the amplitudes of the states $|a\rangle$ and $|b\rangle$ respectively.

Substituting Eq.(C-2) into Eq.(C-1), one gets:

$$C_o E_a|a\rangle + C_o V|a\rangle + D_o E_b|b\rangle + D_o V|b\rangle = E\{C_o|a\rangle + D_o|b\rangle\} \tag{C-3}$$

where E_a and E_b are the eigenvalues of H_o for the eigenstates $|a\rangle$ and $|b\rangle$, respectively.

Multiplying both sides of Eq.(C-3) by the state vector $\langle a|$ and integrating over all space one gets

$$C_o E_a' + D_o V_{ab} = C_o E \tag{C-4}$$

and similarly, if one multiplies Eq.(C-3) by $\langle b|$ and integrates over all space, one obtains:

$$C_o V_{ba} + D_o E_b' = D_o E \tag{C-5}$$

where

$$E_a' = E_a + \langle a|V|a\rangle$$

$$E_b' = E_b + \langle b|V|b\rangle$$

and

$$V_{ij} = \langle i|V|j\rangle \; ; \quad i, j = a, b$$

Equation (C-4) and Eq.(C-5) can be written as a matrix equation:

$$\begin{pmatrix} E_a' - E & V_{ab} \\ V_{ba} & E_b' - E \end{pmatrix} \begin{pmatrix} C_o \\ D_o \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{C-6}$$

A non-trivial solution of this equation exists, if the determinant of the matrix

$$\begin{pmatrix} E_a' - E & V_{ab} \\ V_{ba} & E_b' - E \end{pmatrix}$$

is zero. This gives

$$(E_a' - E)(E_b' - E) - |V_{ab}|^2 = 0 \tag{C-7}$$

The two roots of this equation, are the energy eigenvalues of the Hamiltonian $\mathcal{H}$:

$$\left.\begin{matrix} E_1^{\circ} \\ E_2^{\circ} \end{matrix}\right\} = (E_a'+E_b')/2 \pm \tfrac{1}{2}(\Delta^2+4V^2)^{1/2} \tag{C-8}$$

where

$$\Delta = E_a' - E_b'$$

and

$$V^2 = |V_{ab}|^2 .$$

The eigenstates of the Hamiltonian $\mathcal{H}$ are obtained by substituting the energy eigenvalues of $\mathcal{H}$ from Eq.(C-8) into Eq.(C-6) and solving for the coefficients C_o and D_o.

The normalised eigenstates of $\mathcal{H}$ are:

$$|1\rangle = C_o^{(1)}|a\rangle + D_o^{(1)}|b\rangle$$

and (C-9)

$$|2\rangle = C_o^{(2)}|a\rangle + D_o^{(2)}|b\rangle$$

where

$$C_o^{(1)} = 1/\sqrt{2}\,(1+\Delta/\sqrt{\Delta^2+4V^2})^{1/2}$$

$$D_o^{(1)} = 1/\sqrt{2}\,(1-\Delta/\sqrt{\Delta^2+4V^2})^{1/2}$$

$$C_o^{(2)} = -D_o^{(1)} \tag{C-10}$$

and

$$D_o^{(2)} = C_o^{(1)} .$$

APPENDIX D

Matrix Elements of the Hyperfine Interaction H_D and the Nuclear Quadrupole Interaction H_Q in Li^7

The Hamiltonian for the hyperfine interaction is defined in Eq.(4-13) as:

$$H_D = \alpha \left[\frac{\vec{l} - \vec{s}}{r^3} + 3\,\frac{(\vec{s}\cdot\vec{r})\vec{r}}{r^5} \right]\cdot\vec{I} + \xi\, \vec{s}\cdot\vec{I}$$

This Hamiltonian can be written (14) in the following way

$$H_D = \frac{\alpha}{r^3}\left[\vec{l}\cdot\vec{I} + \sqrt{\frac{24\pi}{5}} \sum_{m_1, m_2} (-1)^{m_1+m_2}\, C(112, m_1 m_2)\, Y_2^{m_1+m_2}(\hat{r}) \right.$$

$$\left. \times\, T_1^{-m_1}(s)\, T_1^{-m_2}(I) \right] + \xi\, \vec{s}\cdot\vec{I} \qquad \text{(D-1)}$$

where $C(112, m_1 m_2)$ are the Clebsch-Gordan coefficients, $Y_2^{m_1+m_2}(\hat{r})$ are the spherical harmonics of rank two and T_1 is an irreducible tensor of rank one.

The matrix elements of H_D between the two states $|\phi_4, m_I\rangle$ and $|\phi_6, m_I\rangle$ is obtained as follows:

$$\langle 3/2\; m_I' | \langle \phi_4 | H_D | \phi_6 \rangle | 3/2\; m_I \rangle$$

$$= C_0\, {}_I\langle 3/2\; m_I' |\, {}_l\langle 1\,-1 |\, {}_s\langle 1/2\,-1/2 | H_D | 1/2\,-1/2 \rangle_s | 1\,0 \rangle_l | 3/2\; m_I \rangle_I$$

$$- D_0\, {}_I\langle 3/2\; m_I' |\, {}_l\langle 1\,-1 |\, {}_s\langle 1/2\,-1/2 | H_D | 1/2\; 1/2 \rangle_s | 1\,-1 \rangle_l | 3/2\; m_I \rangle_I$$

$$= C_o \alpha \langle \frac{1}{r^3} \rangle \Big[\langle 3/2\, m_I' | \langle 1 -1 | \, l_z I_z + \frac{1}{2}(l_+ I_- + l_- I_+) \, | 1 0 \rangle | 3/2\, m_I \rangle$$

$$+ \sqrt{24\pi/5} \sum_{\substack{m_1 \\ m_2}} (-1)^{m_1+m_2} C(112, m_1 m_2) \langle 1 -1 | Y_2^{m_1+m_2}(\hat{r}) | 1 0 \rangle$$

$$\times \langle 1/2 -1/2 | T_1^{-m_1} | 1/2 -1/2 \rangle \langle 3/2\, m_I' | T_1^{-m_2} | 3/2\, m_I \rangle \Big]$$

$$- D_o \alpha \langle \frac{1}{r^3} \rangle \sqrt{24\pi/5} \sum_{m_1 m_2} (-1)^{m_1+m_2} C(112, m_1 m_2) \langle 1 -1 | Y_2^{m_1+m_2}(\hat{r}) | 1 -1 \rangle$$

$$\times \langle 1/2 -1/2 | T_1^{-m_1} | 1/2\, 1/2 \rangle \langle 3/2\, m_I' | T_1^{-m_2} | 3/2\, m_I \rangle - D_o \xi \langle 1/2 -1/2 | \langle 3/2\, m_I' | S_z I_z$$

$$+ \frac{1}{2}(S_+ I_- + S_- I_+) | 1/2\, 1/2 \rangle | 3/2\, m_I \rangle \qquad \text{(D-2)}$$

The matrix elements of $Y_2^{m\ell}(\hat{r})$ and T_1^m are obtained by using the Wigner-Eckart Theorem (15)

$$\langle \ell_f m_f | T_1^m(\ell) | \ell_i m_i \rangle = C(\ell_i 1 \ell_f, m_i m m_f) \sqrt{\ell_i(\ell_i+1)}\, \delta_{\ell_f \ell_i}$$

$$\langle \ell_f m_f | Y_\ell^m | \ell_i m_i \rangle = C(\ell_i \ell \ell_f, m_i m m_f) C(\ell_i \ell \ell_f, 000)$$

$$\times \sqrt{\frac{(2\ell_i+1)(2\ell+1)}{4\pi(2\ell_f+1)}} \qquad \text{(D-3)}$$

Thus, using Eq.(D-3) and the values of the Clebsch-Gordon coefficients, one obtains from Eq.(D-2)

$$\langle \phi_4, m_I | H_D | \phi_6, m_I' \rangle = \frac{1}{2} \Big[\frac{1}{5} \left(\frac{7}{\sqrt{2}} C_o - D_o \right) \alpha \langle \frac{1}{r^3} \rangle$$

$$- D_o \xi \Big] \sqrt{(5/2 - m_I)(3/2 + m_I)}\; \delta_{m_I' \, m_I - 1} \qquad \text{(D-4)}$$

The diagonal matrix element of H_D in state $|\phi_4, m_I\rangle$ is:

$$\langle \phi_4, m_I | H_D | \phi_4, m_I\rangle = \alpha \langle \tfrac{1}{r^3}\rangle \langle 3/2\, m_I | \langle 1/2\, -1/2 | \langle 1\, -1 \,| l_z I_z$$

$$+ \tfrac{1}{2}(l_+ I_- + l_- I_+) | 1 -1\rangle | 1/2 -1/2\rangle | 3/2\, m_I\rangle$$

$$+ \alpha \langle \tfrac{1}{r^3}\rangle \sqrt{24\pi/5} \sum_{m_1, m_2} (-1)^{m_1+m_2} C(112, m_1 m_2) \langle 1 -1 | Y_2^{m_1+m_2}(\hat{r}) | 1 -1\rangle$$

$$\times \langle 1/2 -1/2 | T_1^{-m_1} | 1/2 -1/2\rangle \langle 3/2\, m_I | T_1^{-m_2} | 3/2\, m_I\rangle$$

$$+ \xi \langle 1 -1 | \langle 1/2 -1/2 | \langle 3/2\, m_I | S_z I_z + \tfrac{1}{2}(S_+ I_- + S_- I_+) | 1 -1\rangle | 1/2 -1/2\rangle | 3/2\, m_I\rangle$$

which , after substituting the different matrix elements of Y_2 and T_1 and Clebsch-Gordon coefficients, reduces to

$$\langle \phi_4, m_I | H_D | \phi_4, m_I\rangle = -\tfrac{4}{5}\, m_I \alpha \langle \tfrac{1}{r^3}\rangle - \tfrac{1}{2} m_I \xi \quad \text{(D-5)}$$

Similarly, the following matrix elements of H_D are obtained:

$$\langle 3/2\, m_I | \langle 1/2 -1/2 | \langle 1 -1 | H_D | 1 -1\rangle | 1/2\, 1/2\rangle | 3/2\, m_I\rangle = -\tfrac{6}{5} m_I \alpha \langle \tfrac{1}{r^3}\rangle$$
$$+ m_I \xi / 2$$

$$\langle 3/2\, m_I | \langle 1/2 -1/2 | \langle 1 0 | H_D | 1 0\rangle | 1/2 -1/2\rangle | 3/2\, m_I\rangle = -\tfrac{2}{5} m_I \alpha \langle \tfrac{1}{r^3}\rangle$$
$$- m_I \xi / 2 \quad \text{(D-6)}$$

and

$$\langle 3/2\, m_I | \langle 1/2\, 1/2 | \langle 1 -1 | H_D | 1 0\rangle | 1/2 -1/2\rangle | 3/2\, m_I\rangle$$

$$= \langle 3/2\, m_I | \langle 1/2 -1/2 | 1 0 | H_D | 1 -1\rangle | 1/2\, 1/2\rangle | 3/2\, m_I\rangle$$

$$= (3/5\sqrt{2})\, m_I\, \alpha \langle 1/r^3\rangle \quad \text{(D-7)}$$

Thus, using Eq.(D-6) and Eq.(D-7), the diagonal matrix element of H_D in state $|\phi_6, m_I\rangle$ is

$$\langle \phi_6, m_I | H_D | \phi_6, m_I \rangle = -\frac{1}{5}\left(6 D_o^2 + 2C_o^2 + \sqrt{2}\cdot 3 C_o D_o\right) m_I \alpha \langle \tfrac{1}{r^3} \rangle$$

$$+ \frac{1}{2}\left(D_o^2 - C_o^2 \right) m_I \xi \quad . \qquad \text{(D-8)}$$

The nuclear electrostatic quadrupole interaction is

$$H_Q = -e^2 Q \left[\frac{3I_z^2 - I^2}{4I(2I-1)} \right] \cdot \left(\frac{3\cos^2\theta - 1}{r^3} \right)$$

$$= -e^2 Q \left[\frac{3I_z^2 - I^2}{4I(2I-1)} \right] 4\sqrt{\frac{\pi}{5}}\, \frac{Y_2^0(\hat{r})}{r^3} \quad .$$

Using Eq.(D-3), the matrix elements of H_Q are written as:

$$\langle \phi_4, m_I | H_Q | \phi_4, m_I' \rangle = \frac{b}{4}\left(m_I^2 - 5/4 \right) \delta_{m_I m_I'} \qquad \text{(D-9)}$$

and

$$\langle \phi_6, m_I | H_Q | \phi_6, m_I' \rangle = \frac{b}{4}\left(D_o^2 - 2C_o^2 \right)\left(m_I^2 - 5/4 \right) \delta_{m_I m_I'}$$

(D-10)

where

$$b = \frac{2}{5} e^2 Q \langle 1/r^3 \rangle$$

and C_o and D_o are defined in Eq.(4-12).

The experimental value of b for Li^7 (13) is

$$b = -0.18 \pm 0.12 \ \text{Mc/sec} \ . \qquad \text{(D-11)}$$

APPENDIX E

Some Useful Matrix Elements of $\vec{p}\cdot\hat{e}_\lambda$

The matrix elements of $\vec{p}\cdot\hat{e}_\lambda$ for different excited states and ground states are calculated and the products $p^{\lambda}_{c'\mu}p^{\lambda *}_{c'\mu'}p^{\sigma}_{\mu c}p^{\sigma *}_{\mu' c}$ are computed.

For $\mu = 1$ and $\mu' = 3$, one gets from Eq.(4-17)

$$p^{\lambda}_{c'1} = C_1 \langle c' | \vec{p}\cdot\hat{e}_\lambda | \phi_4, 3/2 \rangle + D_1 \langle c' | \vec{p}\cdot\hat{e}_\lambda | \phi_6, 1/2 \rangle$$

$$p^{\lambda *}_{c'3} = C_2 \langle \phi_4, 1/2 | \vec{p}\cdot\hat{e}_\lambda | c' \rangle + D_2 \langle \phi_6, -1/2 | \vec{p}\cdot\hat{e}_\lambda | c' \rangle .$$

The matrix element $p^{\lambda}_{c'\mu}$ is equal to zero if the states $|c'\rangle$ and $|\psi_\mu\rangle$ do not have the same m_I. Thus the product $\sum_{c'} p^{\lambda}_{c'1} p^{\lambda *}_{c'3}$ reduces to

$$\sum_{c'} p^{\lambda}_{c'1} p^{\lambda *}_{c'3} = \sum_{c'} C_2 D_1 \langle c' | \vec{p}\cdot\hat{e}_\lambda | \phi_6, 1/2 \rangle \langle \phi_4, 1/2 | \vec{p}\cdot\hat{e}_\lambda | c' \rangle \qquad \text{(E-1)}$$

After writing the matrix elements of $\vec{p}\cdot\hat{e}_\lambda$ in terms of the orbital states $|l m_l\rangle$ of the election, one gets

$$\sum_{c'} p^{\lambda}_{c'1} p^{\lambda *}_{c'3} = C_2 D_1 C_0 \langle 00 | \vec{p}\cdot\hat{e}_\lambda | 10 \rangle \langle 1 -1 | \vec{p}\cdot\hat{e}_\lambda | 00 \rangle \qquad \text{(E-2)}$$

and therefore

$$\sum_{cc'} p^{\lambda}_{c'1} p^{\lambda *}_{c'3} p^{\sigma}_{1c} p^{\sigma *}_{3c} = C_0^2 D_1^2 C_2^2 \langle 00 | \vec{p}\cdot\hat{e}_\lambda | 10 \rangle \langle 1 -1 | \vec{p}\cdot\hat{e}_\lambda | 00 \rangle$$

$$\times \langle 00 | \vec{p}\cdot\hat{e}_\sigma | 1 -1 \rangle \langle 10 | \vec{p}\cdot\hat{e}_\sigma | 00 \rangle \qquad \text{(E-3)}$$

Similarly, one obtains the following set of nonvanishing matrix elements:

$$
\begin{aligned}
&\sum_{cc'} p^{\lambda}_{c'1}\, p^{\lambda *}_{c'4}\, p^{\sigma}_{1c}\, p^{\sigma *}_{4c} = C_0^2 D_1^2 D_2^2 \cdot f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'1}\, p^{\lambda *}_{c'8}\, p^{\sigma}_{1c}\, p^{\sigma *}_{8c} = C_0^2 C_1^2 f^{*} \quad , \\
&\sum_{cc'} p^{\lambda}_{c'2}\, p^{\lambda *}_{c'3}\, p^{\sigma}_{2c}\, p^{\sigma *}_{3c} = C_0^2 C_1^2 C_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'2}\, p^{\lambda *}_{c'4}\, p^{\sigma}_{2c}\, p^{\sigma *}_{4c} = C_0^2 C_1^2 D_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'2}\, p^{\lambda *}_{c'8}\, p^{\sigma}_{2c}\, p^{\sigma *}_{8c} = C_0^2 D_1^2 f^{*} \quad , \\
&\sum_{cc'} p^{\lambda}_{c'3}\, p^{\lambda *}_{c'5}\, p^{\sigma}_{3c}\, p^{\sigma *}_{5c} = C_0^2 C_3^2 D_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'3}\, p^{\lambda *}_{c'6}\, p^{\sigma}_{3c}\, p^{\sigma *}_{6c} = C_0^2 D_3^2 D_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'4}\, p^{\lambda *}_{c'5}\, p^{\sigma}_{4c}\, p^{\sigma *}_{5c} = C_0^2 C_3^2 C_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'4}\, p^{\lambda *}_{c'6}\, p^{\sigma}_{4c}\, p^{\sigma *}_{6c} = C_0^2 D_3^2 C_2^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'5}\, p^{\lambda *}_{c'7}\, p^{\sigma}_{5c}\, p^{\sigma *}_{7c} = C_0^2 D_3^2 f \quad , \\
&\sum_{cc'} p^{\lambda}_{c'6}\, p^{\lambda *}_{c'7}\, p^{\sigma}_{6c}\, p^{\sigma *}_{7c} = C_0^2 C_3^2 f \quad ,
\end{aligned}
\tag{E-4}
$$

where

$$
f = \langle 00|\vec{p}\cdot\hat{e}_{\lambda}|10\rangle\langle 1\,{-1}|\vec{p}\cdot\hat{e}_{\lambda}|00\rangle\langle 00|\vec{p}\cdot\hat{e}_{\sigma}|1\,{-1}\rangle\langle 10|\vec{p}\cdot\hat{e}_{\sigma}|00\rangle \tag{E-5}
$$

and f^{*} is the complex conjugate of f.

For plane polarized beams of the incident and the scattered radiation, the polarization vectors $\hat{e}_{\sigma}$ and $\hat{e}_{\lambda}$ are:

$$\hat{e}_{\sigma} = \hat{z}\cos\theta_a - \hat{y}\sin\theta_a$$

and (E-6)

$$\hat{e}_{\lambda} = \hat{z}\cos\theta_e + \hat{x}\sin\theta_e$$

where θ_a and θ_e are the angles between the plane of polarization and the z- axis for the incident and the scattered beams, respectively.

From Eq.(A-11), the matrix element P^{λ}_{ca} is written as:

$$\langle c|\vec{p}\cdot\hat{e}_{\lambda}|a\rangle = i\omega_0 \langle c|\vec{r}.\hat{e}_{\lambda}|a\rangle$$

where ω_0 is the frequency difference between the two states and $\vec{r}$ is the position vector of the electron.

From Eq.(E-6), the scalar product $\vec{r}\cdot\hat{e}_{\sigma}$ and $\vec{r}\cdot\hat{e}_{\lambda}$ can be written in terms of spherical hermonics of rank one as follows:

$$\vec{r}.\hat{e}_{\sigma} = \frac{4\pi}{3}\, r\sum_{m}(-1)^m Y_1^m(\hat{r})\, Y_1^{-m}(\theta_a, \pi/2)$$

and (E-7)

$$\vec{r}.\hat{e}_{\lambda} = \frac{4\pi}{3}\cdot r\sum_{m}(-1)^m Y_1^m(\hat{r})\, Y_1^{-m}(\theta_e, 0) \ .$$

Thus the matrix element $\langle 00|\vec{p}\cdot\hat{e}_{\lambda}|10\rangle\langle 1-1|\vec{p}\cdot\hat{e}_{\lambda}|0\,0\rangle$ becomes:

$$\langle 00|\vec{p}\cdot\hat{e}_{\lambda}|10\rangle\langle 1-1|\vec{p}\cdot\hat{e}_{\lambda}|00\rangle = -(4\pi/3)^2\,\omega_0^2\,\langle r\rangle^2$$

$$\times\ \langle 00|Y_1^0|10\rangle\langle 1-1|Y_1^{-1}|00\rangle\, Y_1^0(\theta_e, 0)\, Y_1^1(\theta_e\, 0)$$

$$= \frac{\omega_0^2\,\langle r\rangle^2}{3\sqrt{2}}\,\sin\theta_e\cos\theta_e \qquad \text{(E-8)}$$

Similarly

$$\langle 10|\vec{p}\cdot\hat{e}_\sigma|00\rangle\langle 00|\vec{p}\cdot\hat{e}_\sigma|1-1\rangle = -i\,\frac{\omega_0^2\langle r\rangle^2}{3\sqrt{2}}\,\mathrm{Sin}\,\theta_a\,\mathrm{Cos}\,\theta_a\,. \tag{E-9}$$

The quantity f defined in Eq.(E-5) reduces to

$$f = \langle 00|\vec{p}\cdot\hat{e}_\lambda|10\rangle\langle 1-1|\vec{p}\cdot\hat{e}_\lambda|00\rangle\langle 10|\vec{p}\cdot\hat{e}_\sigma|00\rangle\langle 00|\vec{p}\cdot\hat{e}_\sigma|1-1\rangle$$

$$= -i\,\frac{\omega_0^4\langle r\rangle^4}{72}\,\mathrm{Sin}\,2\theta_a\cdot\mathrm{Sin}\,2\theta_e\,. \tag{E-10}$$

This quantity is pure imaginary that means the signal S_C as defined in Eq.(4-30) is pure dispersion as a function of the external magnetic field.

If the beams are unpolarised and have the incidence and scattering directions as shown in Fig. 4-10, then $\vec{r}\cdot\hat{e}_\sigma$ becomes:

$$\sum_{\sigma=1,-1}\vec{r}\cdot\hat{e}_\sigma = \sqrt{\frac{4\pi}{3}}\sum_{\substack{m=-1\\ \sigma=1,-1}}^{1} D^1_{m\sigma}(\phi_1,\theta_1,0)\,r\,Y_1^m(\hat{r})\,. \tag{E-11}$$

Therefore

$$\sum_{\sigma=1,-1}\langle 10|\vec{p}\cdot\hat{e}_\sigma|00\rangle\langle 00|\vec{p}\cdot\hat{e}_\sigma|1-1\rangle = \frac{4\pi}{3}\,\omega_0^2\langle r\rangle^2$$

$$\times\sum_\sigma D^1_{1\sigma}(\phi_1,\theta_1,0)\,D^1_{0\sigma}(\phi_1,\theta_1,0)\langle 00|Y_1^1|1-1\rangle\langle 10|Y_1^0|00\rangle$$

$$= -\omega_0^2\langle r\rangle^2/3\sum_\sigma D^1_{1\sigma}(\phi_1,\theta_1,0)\,D^1_{0\sigma}(\phi_1,\theta_1,0)$$

$$= -\omega_0^2\langle r\rangle^2/3\,.\,\mathrm{Sin}\,\theta_1\,\mathrm{Cos}\,\theta_1\,e^{-i\phi_1}$$

and similarly

$$\sum_\lambda\langle 00|\vec{p}\cdot\hat{e}_\lambda|10\rangle\langle 1-1|\vec{p}\cdot\hat{e}_\lambda|00\rangle = -\omega_0^2\langle r\rangle^2/3\,.\,\mathrm{Sin}\,\theta_2\,\mathrm{Cos}\,\theta_2\,e^{i\phi_2},$$

Hence, for the unpolarized beams of the incident and the scattered light f becames:

$$f = \sum_{\lambda\sigma} \langle 00|\vec{p}\cdot\hat{e}_\lambda|10\rangle\langle 1{-}1|\vec{p}\cdot\hat{e}_\lambda|00\rangle\langle 10|\vec{p}\cdot\hat{e}_\sigma|00\rangle\langle 00|\vec{p}\cdot\hat{e}_\sigma|1{-}1\rangle$$

$$= \frac{\omega_0^4\langle r\rangle^4}{72}\,\mathrm{Sin}2\theta_1\,\mathrm{Sin}2\theta_2\,e^{i(\phi_2-\phi_1)}. \qquad \text{(E-12)}$$