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THEORY OF HYDROGEN LINE BROADENING IN HIGH-TEMPERATURE PARTIALLY IONIZED GASES

AFOSR-TN-57-8
ASTIA Document No. AD 115 040

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Project 2189

OFFICE OF SCIENTIFIC RESEARCH, U. S. AIR FORCE
AIR RESEARCH AND DEVELOPMENT COMMAND
PROJECT NO. R-357-40-6, CONTRACT NO. AF 18(600)-983

March 1957

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ABSTRACT

The purpose of this investigation is to study theoretically the broadening of the hydrogen Balmer lines observed in the radiation of high-temperature partially ionized gases. The theory is based on the classical path approximation for the motion of the perturbers. The general problem of the broadening of a group of lines arising from transitions between "nearly degenerate" states is considered. The method employed is not restricted by the usual assumption of binary collision. The formalism is subsequently specialized to the case where the broadening due to the interactions between an ensemble of ions and a hydrogen atom can be treated as a static perturbation. The validity of this approximation is discussed in detail. The static ion field removes the normal degeneracy of the states of the hydrogen atom. The high-velocity electrons present in the electrically neutral plasma are then shown to cause phase changes and transitions between these nearly degenerate states. The phase shifts due to adiabatic effects and the collision-induced transitions due to nonadiabatic effects are of comparable importance as sources of broadening by electrons. The resultant profile caused by the electron-atom collisions is then averaged over the static ion field splitting with the Holtsmark distribution function. Series expansions for the line profile are obtained which reduce to the Holtsmark expansion for zero electron density and to the dispersion distribution for zero ion density.

The principal result of these calculations is that both ions and electrons must be taken into account in the derivation of Balmer line absorption coefficients. This result is confirmed by experiments in the Shock Tube Laboratory at The University of Michigan (E. B. Turner, Dissertation, 1956; see also ASTIA Document No. AD 86309, Univ. of Mich., Eng. Res. Inst.).

The broadening of the Lyman alpha line by electron collisions is considered in detail for comparison with other theories. For this line, the nonadiabatic and the adiabatic effects are found to contribute in the ratio one to two to the broadening.

OBJECTIVE

The objective of research under ARDC Contract No. AF 18(600)-983 is the study of the hydrodynamics of and the spectra behind strong shock waves produced in a shock tube.

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   O.A.: Engineering Research Institute, The University of Michigan
   M.A.: Office of Scientific Research

2. Originating agency and/or monitoring agency report number:

   O.A.: ERI Report No. 2189-3-T
   M.A.: OSR-TN-57-8

3. Title and classification of title: Theory of Hydrogen Line Broadening in High-Temperature Partially Ionized Gases (UNCLASSIFIED)

4. Personal author: Kolb, Alan C. (Otto Laporte, Project Supervisor)

5. Date of report: March 1957

6. Pages: 167

7. Illustrative material: 2 Tables, 9 Figures

8. Prepared for Contract No. AF 18(600)-983

9. Prepared for Project Code(s) and/or No.(s): R-357-40-6

10. Security classification: UNCLASSIFIED

11. Distribution limitations: See Distribution List

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CHAPTER I

INTRODUCTION

This theoretical investigation of the broadening of hydrogen lines in a high-temperature, partially ionized gas was motivated by experiments performed in the Shock-Tube Laboratory at The University of Michigan.*[1-4] These experiments showed that the broadening of the Balmer line H_β was greater than that predicted by the familiar Holtsmark[5-7] statistical theory for broadening by static ion fields. In this dissertation the additional broadening due to high-velocity plasma electrons is calculated in the classical path approximation.** It will be shown that the electron broadening is comparable to the ion broadening at all densities and cannot be neglected in a theoretical description of hydrogen line profiles. An extensive comparison between the theory and the experiments has not yet been carried out. However, the main features of the theory are confirmed by the existing data and it is probable that the additional broadening observed can be ascribed to the presence of electrons.

The general conclusion that plasma electrons are an important source of broadening of hydrogen lines is of some importance to astrophysics. Until recently, hydrogen line profiles in stellar spectra have been analyzed on the basis of the Holtsmark theory.[5-7] From these calculations one may derive the electron pressure and temperature structure of stellar

*These experiments were carried out by E. B. Turner and L. Doherty under the supervision of Professor Otto Laporte.

**The perturber trajectories are treated classically.

envelopes. Application of the theory developed in this dissertation to problems of this type by Aller, Jugaku and Elste[8] modifies in a non-trivial way the calculated pressure-temperature distribution in a typical stellar atmosphere.

A survey of the existing literature on line broadening revealed that there was no theory available with which one could calculate a Balmer line broadened by both ions and electrons. An early theory by Spitzer[9-11] was restricted to Lyman α since it did not take into account degenerate ground states. Furthermore, this theory was based on the binary collision assumption and did not take into account the simultaneous broadening by both ions and electrons. The results of Section III.15 constitute a generalization of the Spitzer theory that is applicable to Balmer line broadening by electrons moving in a static ion field. The resulting profile is then averaged over the static field with the Holtsmark probability distribution. Other calculations[10-12] of electron broadening in the classical path approximation either neglected nonadiabatic transitions or else took them into account by rough order-of-magnitude estimates. These various theories will be discussed in Chapter IV and compared with the theory developed in Chapter III and Chapter V.

Chapter II contains a brief survey of hydrogen line broadening experiments with shock tubes and high-temperature arcs. In Chapter III the classical path theory is discussed in detail. Much of this material is more or less well known. For example, the adiabatic theory has received much attention by many authors. Our contribution to this topic is a new presentation in Section III.12 and III.13 of the validity criteria for the phase-shift and statistical approximations. Sections III.1-8 and III.10-11 contain background material necessary for subsequent calcula-

tions. This includes a discussion of the validity of the classical path approximation, the Stark effect in static homogeneous electric fields, the Fourier integral expression for the line shape,* the principle of detailed balance, the adiabatic approximation, and the method of averaging over collisions. In Section III.9 an expression for the time-dependent dipole matrix element $\mu^{c}_{a\alpha}(t)$ is obtained using first-order perturbation theory. This result is used in Section III.14 to derive the frequency distribution of spectral lines arising out of transitions between degenerate initial and final states. This formula was obtained earlier by Anderson,[14] who considered the pressure broadening of microwave and infrared lines. Our derivation differs from Anderson's and does not contain the assumption that the average duration of each collision is small compared to the average time between collisions. For long-range forces the binary collision assumption fails, so this generalization is important for hydrogen line broadening by fast plasma electrons. In Section III.15 a theory of the line wing is developed for the case where a line is composed of a composite of lines arising out of transitions between nearly degenerate initial and final states. This investigation was carried out because the statistical theory is valid for calculating the influence of the ion fields on the line wing. The static ion fields remove the normal hydrogen degeneracy so that the plasma electrons interact with nearly degenerate hydrogen atoms.

Chapter V contains a detailed application of the formal results of Chapter III to the hydrogen lines. The electron broadening of Lyman α was worked out in detail in Section V.7 as an example. It was found that the nonadiabatic contribution gives rise to two-thirds of the electron

*This discussion follows that of Bloom and Margenau, Ref. 13.

broadening of this line. These results are compared with a recent quantum mechanical theory[15] in Section V.8.

In Section V.2-6 the validity range of the theory is discussed further with numerical examples, errors in the velocity average are calculated, the Debye cutoff is introduced,[16] the effect of close collisions is taken into account, the adiabatic theory of electron broadening is analyzed in detail, and new results are obtained for the adiabatic contribution to the line shape. In Sections V.10 and V.12 the simultaneous effect of both ions and electrons is calculated. Series expansions for the line profile are obtained which reduce to the Holtsmark distribution for zero electron density and to the dispersion distribution for zero ion density. Sections V.11-15 contain a discussion of the relative importance of ion and electron broadening, nonadiabatic broadening by electrons, a preliminary comparison of the theory with experiment, and finally some remarks on unsolved problems connected with hydrogen line broadening in partially ionized gases.

CHAPTER II

SURVEY OF THE EXPERIMENTAL SITUATION

1. Shock-Tube Experiments

Before taking up the theoretical problem of calculating hydrogen line profiles, a short résumé of the experiments which stimulated this research will be presented. Our attention will be focused mainly on experiments pertaining to hydrogen line broadening in partially ionized gases.

High-temperature spectra can be obtained in the laboratory by a variety of techniques. However, of these the shock tube and certain arc sources provide convenient means of obtaining fundamental data on line broadening in high-temperature gases. In this chapter the results of shock-tube experiments will be briefly outlined. Recent arc data from Kiel University will also be discussed and compared qualitatively with the shock-tube results.

The shock tube provides a homogeneous high-temperature light source in thermal equilibrium with which one can measure spectral line shapes under known conditions in a luminous gas. The shock tube constructed by E. B. Turner[1] at The University of Michigan will be briefly described. This shock tube consists of a high-pressure chamber containing a gas (usually hydrogen and referred to as the driver gas) at pressures up to 135 atmospheres, separated by a diaphragm from a low-pressure chamber containing a gas (usually one of the rare gases) at a few mm Hg pressure. A very strong shock wave is generated when the diaphragm is broken. The

gas behind this shock wave travels down the tube at a high velocity. When the incident shock wave reflects from the end of the tube, the gas behind it is brought to rest. The conversion of the kinetic energy of ordered motion into thermal energy heats the gas behind the reflected shock wave. By this means, temperatures up to 15,000°K can be easily produced in the gas which was initially in the low-pressure chamber.*

The spectrum of the luminous gas is observed at the end of the shock tube in the region behind the reflected shock wave. Since the luminosity is a transient phenomenon, it is desirable to measure the spectra as a function of time. This is achieved by moving a film placed in the focal plane of a spectrograph. The details of these experiments have been presented in a dissertation by Turner.[1]

In order to study the Balmer lines, a small amount of hydrogen was introduced into the low-pressure chamber together with the rare gas, neon.** The Balmer lines H_α, H_β, H_γ, and H_δ have been observed in this way with widths ranging up to several hundred Angstroms, depending on the strength of the shock wave. The neon lines appear sharp in contrast to the hydrogen lines because hydrogen exhibits a first-order Stark effect, while neon does not. It is also observed that alternate members of the Balmer series exhibit a double maximum. Figure 1*** shows a typical spectrum of the Balmer lines H_β, H_γ, and H_δ, which illustrates this behavior. The double maximum in H_δ is clearly in evidence. H_β is overex-

*Still higher temperatures can be obtained when an explosive mixture of hydrogen and oxygen is ignited in the high-pressure chamber.

**Temperatures up to 15,000°K can be reached in neon with very little continuum because of the high (21.5 ev) ionization potential of neon.

***Taken from page 107, Ref. 1.

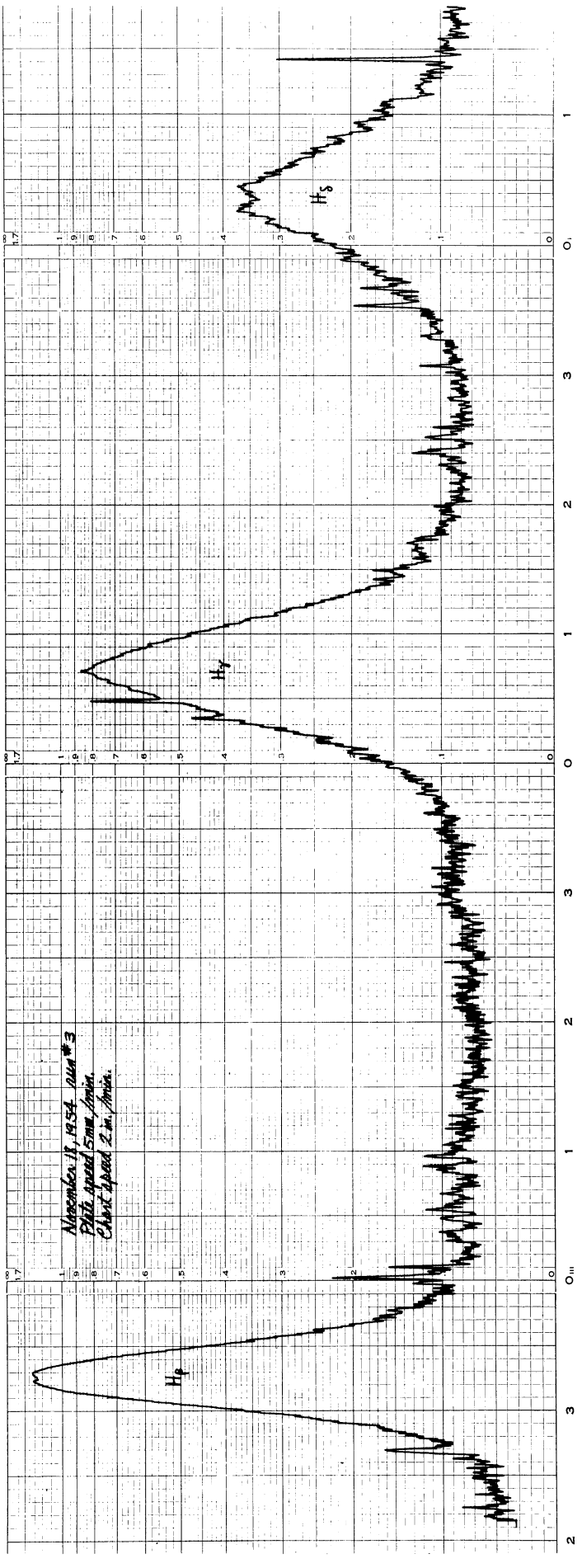


Figure 1. Shock-tube spectra of the Balmer lines H_β, H_γ, H_δ.

posed. In Figure 2* a spectrum of H_β as a function of time at a fixed position in the tube behind the reflected shock wave is shown. The constant width over 100 μsec indicates that the ion density is constant within this time interval, implying that thermal equilibrium has been established. The double maximum is clearly present in this spectrum. The presence of a double maximum is to be expected from the selection rules for hydrogen and the theory of the Stark effect since the odd members of the Balmer series, i.e., H_β, H_δ, etc., have no central Stark component in an electric field. The absence of a central Stark component in the shock-tube spectra demonstrates the existence of a first-order Stark effect due to the presence of local electric fields of ions and electrons.

These general features have also been observed in the Oklahoma and Cornell shock tubes. In Fowler's shock tube at Oklahoma, temperatures up to 30,000°K have been reported.[17-22] These high temperatures are produced behind shock waves generated by a high-voltage, low-inductance, electric discharge in hydrogen. Some recent experiments, initiated by the author[23] at the Naval Research Laboratory, indicate that still higher temperatures can be attained in shock tubes of this general type. It is also possible to study the high-temperature spectra of pure low-molecular-weight gases (such as hydrogen or helium) by detonating high explosives in an atmosphere composed of the gas of interest. Seay and Seely[24] at Los Alamos studied helium line profiles and line shifts with a shock tube of this type at temperatures near 20,000°K with ion densities up to 10^{18} cm^{-3}.

In addition to the great broadening of the hydrogen lines, the lines of the rare gases used in the low-pressure chamber of the shock tube are

*Taken from page 115, Ref. 1.

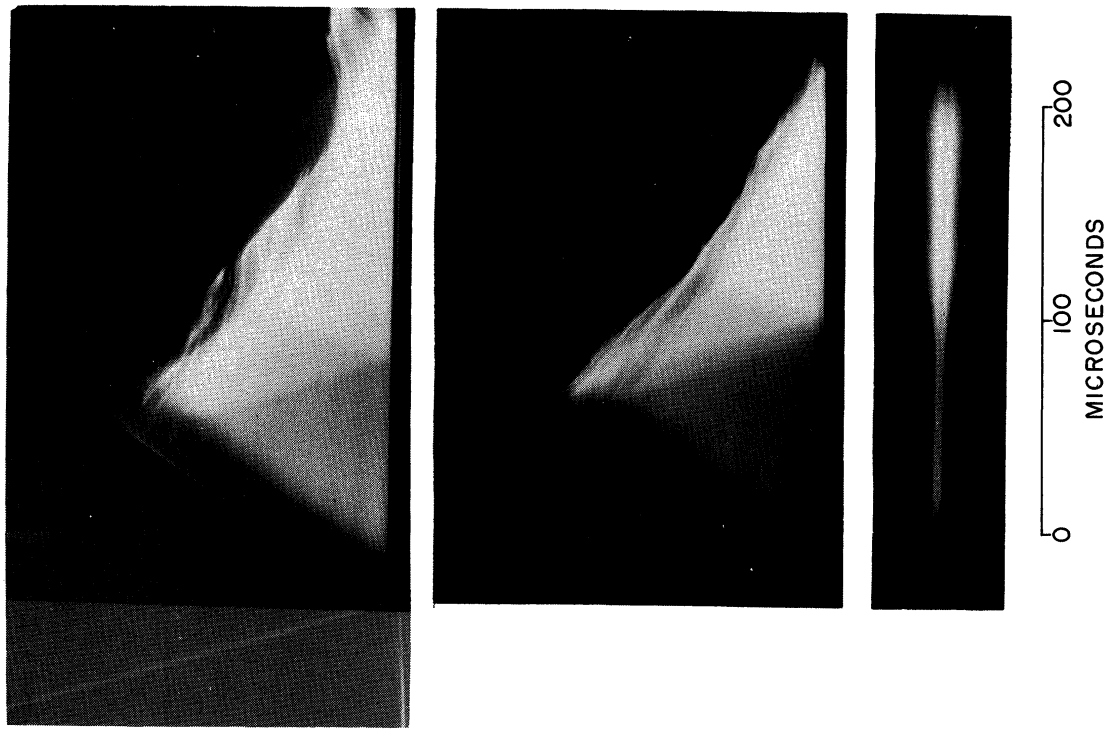


Figure 2. Time-resolved spectrum of H_β with corresponding wave-speed photographs of the primary and reflected shock waves. The left-hand wave-speed photograph was exposed with white light and the center with only the light of H_β.

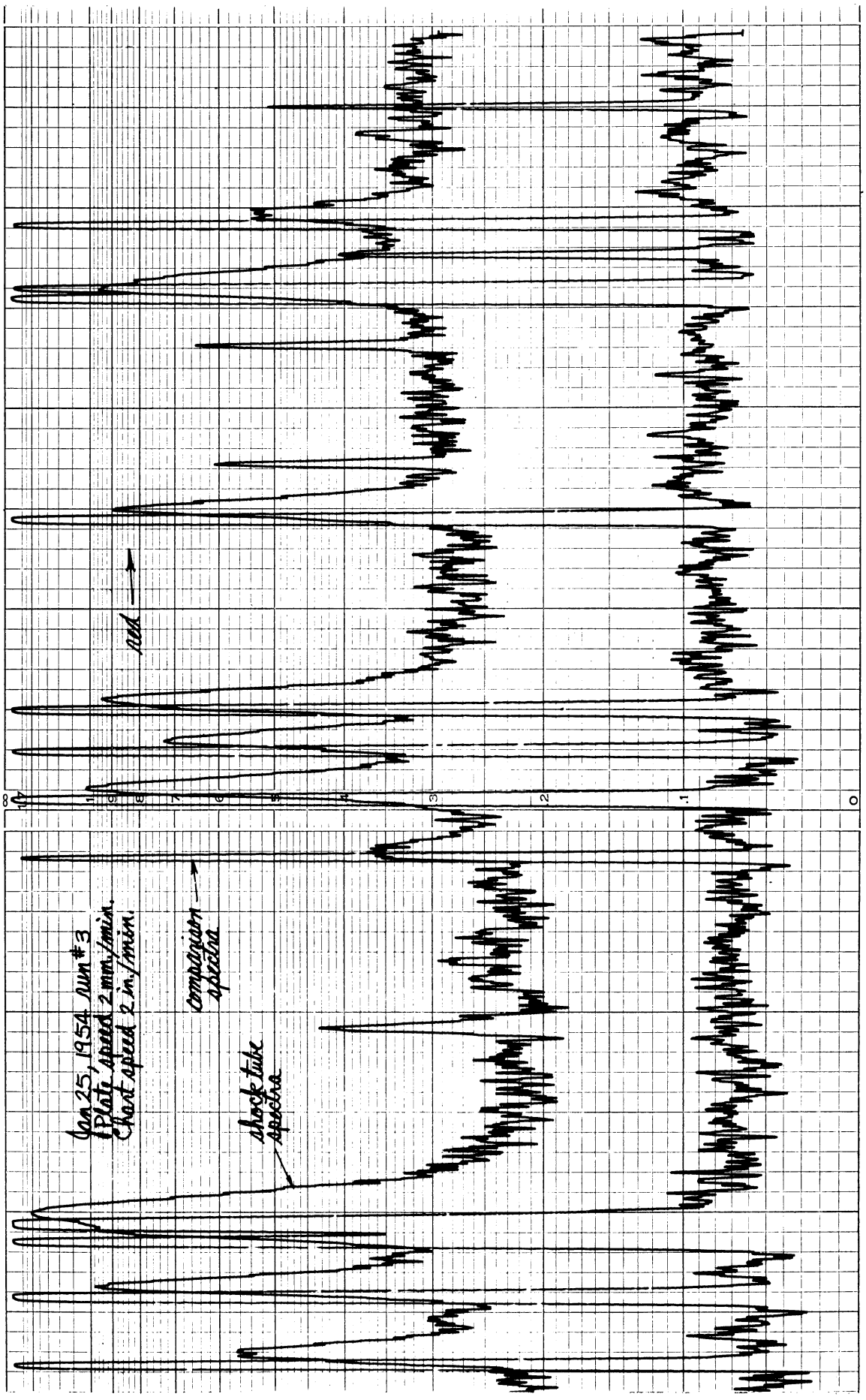
seen to be broadened and generally shifted to the red by perturbations proportional to the square of the instantaneous local electric fields. For example, half-widths and shifts of the order of 3Å are observed in the argon lines at ion densities in the neighborhood of 2×10^{17} cm^{-3}. Figure 3* shows a typical spectrum of argon lines shifted and broadened in the shock tube. The broadening in this case is attributed to the second-order Stark effect due to the local electric fields of neighboring ions and electrons. Further experiments are needed to establish conclusively the frequency distribution in spectral lines broadened by the second-order Stark effect. An investigation of the red asymmetry present in many of the rare-gas lines would be of especial interest and should have a direct relation to the ion density.

2. High-Temperature Arc Experiments

It should be mentioned that hydrogen lines broadened by the Stark effect have also been observed in arc spectra. Special attention will be given here to the extensive experiments with a water-stabilized arc performed at Kiel University by Professor Lochte-Holtgreven and his coworkers.[11,25-30] In this work temperatures of 12,000°K and ion densities of 5×10^{17} cm^{-3} can be easily maintained by circulating a stream of water about an arc column. The Balmer line profiles obtained in this way are in general similar to profiles obtained in the shock tube;** however, there seem to be certain slight differences. The arc profiles do not exhibit the H_δ double maximum, while this feature is definitely present

*Taken from page 100, Ref. 1.

**See Chapter IV, Section 2, for detailed comparison with an H_β profile.



meter trace of asymmetrical

in the shock-tube profiles. It also appears that the dip between the central maxima in H_β is more pronounced in the shock-tube spectra compared to the arc spectra. One interpretation of these differences is that the shock tube provides a more homogeneous light source than does the water-stabilized arc. In any event, the shock tube may be used to verify and supplement conclusions reached at Kiel. At the present time, the Balmer line profiles obtained by photographic photometry at Kiel are more accurate than those obtained in the shock tube because longer exposure times are possible with a continuously burning arc.* However, the shock tube has the advantage that the ion density in the luminous gas may be calculated from hydrodynamic considerations. Therefore, various theoretical results can be compared directly with observations in which the ion density is a fixed parameter. From such experiments it was concluded that ion broadening alone does not account for the width of H_β in shock-tube spectra, and, in agreement with the conclusions of Griem[11] (based on arc data), one must take into account the broadening due to fast electrons present in a neutral plasma. These observations are in general agreement with the theoretical results obtained in subsequent chapters.[31]

*The luminosity in the shock tube lasts a few hundred microseconds.

CHAPTER III

THEORY

1. The Classical Path Theory of Line Broadening

In this chapter those aspects of the classical path approximation to the theory of line broadening which are germane to the problem of hydrogen line broadening by ions and electrons will be discussed in detail. In the classical path approximation it is assumed that a quantum mechanical system (atom or molecule) is perturbed by neighboring particles whose trajectories may be described classically. This approximation has received much attention in the literature, particularly in the adiabatic limit where the effect of collision-induced transitions in the radiating atom or molecule are neglected. However, this approximation has no justification for hydrogen atoms perturbed by high-velocity electrons, as will be shown later. Nonadiabatic effects, which involve collision-induced transitions, have been considered by Anderson[14] for radiation arising from transitions between degenerate states with application to the problem of pressure broadening in the microwave and infrared regions of the spectrum. Anderson's theory is restricted to the case where the duration of each collision is much less than the mean time between collisions so that only binary collisions are important. The binary collision assumption should be viewed with caution when long-range interactions cause the broadening, as is the case for hydrogen lines broadened by ions and electrons. A more detailed critique of other theories will be contained in Chapter IV in order to facilitate a comparison with the results of this chapter.

The theory of the broadening of hydrogen lines is complicated by the fact that both ions and electrons must be considered in different approximations. The ions move so slowly that they may be considered to be static (statistical approximation). The electrons, on the other hand, move so fast that one may neglect the duration of each collision (impact and phase-shift approximations).* A discussion of the validity of these approximations will be presented in this chapter and also in Chapter V, where numerical examples will be given. The theory is further complicated by the fact that the "static" ions remove the normal hydrogen degeneracy by the first-order Stark effect. In Section 15 of this chapter nonadiabatic effects in nearly degenerate systems will be considered. The results of this section constitute a generalization of an earlier theory due to Spitzer,[9] who considered the transition region between the statistical and impact approximations. This phase of the theory is still incomplete, however, because of mathematical difficulties which arise near resonance (i.e., near the line center).

2. The Validity of the Classical Path Approximation

In the classical path approximation to the theory of spectral line broadening, the simplifying assumption is made that the Hamiltonian may be expressed as a perfectly definite function of the perturbing particle coordinates which depend on time. It is further assumed in practical calculations that the particles move along prescribed trajectories with constant velocity (see the next section). Because of this latter assumption, one cannot treat by the classical path approximation inelastic collisions which involve a large fraction of the kinetic energy of the relative motion

*This does not mean that one must necessarily restrict the theory to binary electron-atom collisions. The phase-shift approximation is discussed in detail in III.13.

of the perturber and radiator.

In order to talk about an individual ion or electron at all, it is required that the gas be nondegenerate. The familiar Sommerfeld criterion for nondegenerate gases is

$$\bar{\lambda}\, N^{1/3} \ll 1 \,, \tag{3-2.1}$$

where N is the number of particles per cubic centimeter and $\bar{\lambda}$ is the mean de Broglie wavelength

$$\bar{\lambda} = \frac{\hbar}{(2mkT)^{1/2}} \,. \tag{3-2.2}$$

Since the mean distance between particles, $\bar{r}$, is of the order $N^{-1/3}$, the inequality (3-2.1) may be written

$$\bar{\lambda} \ll \bar{r} \sim N^{-1/3} \,. \tag{3-2.3}$$

The Sommerfeld criterion for nondegenerate gases simply states that the mean de Broglie wavelength be much less than the mean distance between particles. Substituting (3-2.2) into this inequality gives

$$m \gg \frac{\hbar^2 N^{2/3}}{2kT} \sim \frac{\hbar^2 (\bar{r})^{-2}}{2kT} \,. \tag{3-2.4}$$

In a typical case of astrophysical interest the temperature is of the order 10^{4}°K. For ion and electron densities in the range $N = 10^{12} - 10^{18}$ cm^{-3}, the inequality (3-2.4) becomes

$$m \gg (10^{-37} - 10^{-33}) \text{ gm.} \tag{3-2.5}$$

This inequality is clearly satisfied by both electrons and ions.

Now since the de Broglie wavelength $\bar{\lambda}$ is approximately $\hbar/m\bar{v}$, (3-2.3) may also be written

$$m\bar{v}\bar{r} \gg \hbar \,. \tag{3-2.6}$$

This inequality expresses the fact that the angular momentum corresponding to collisions with impact parameters near the mean distance between particles must be much greater than the unit of angular momentum $\hbar$. For long-

range Coulomb forces it is just these collisions that are mainly responsible for hydrogen line broadening by electrons. For large quantum numbers one may replace the angular momentum $\ell\hbar$ by the classical angular momentum mvr. The quantum number $\bar{\ell}$ corresponding to the conditions of temperature and density mentioned earlier is

$$\bar{\ell} = \frac{m\bar{v}\bar{r}}{\hbar} \sim \frac{m\bar{v}N^{-1/3}}{\hbar} = 5000 - 50 \,. \tag{3-2.7}$$

With such large quantum numbers it is not unreasonable to treat such collisions classically.

These inequalities also satisfy the validity requirement of the WKB approximation to the wavefunction describing a passing perturber. If the perturber interacts with its neighbors by an interaction of the type

$$V(r) = \text{constant}/r^n \,, \tag{3-2.8}$$

then it is required that the change in V(r) be small over a de Broglie wavelength

$$\left[\lambda \cdot \frac{\frac{\partial V(r)}{\partial r}}{V(r)}\right]_{\text{Avg}} \ll 1 \tag{3-2.9}$$

or

$$\bar{\lambda} \ll \frac{\bar{r}}{n} \,. \tag{3-2.10}$$

Foley[32] has shown in some detail that a wave mechanical treatment of the perturbers in the WKB approximation leads to the classical path theory of line broadening if the classical angular momentum mvr is substituted for $\ell\hbar$.

From these considerations it appears that the classical path approximation may be employed for the calculation of hydrogen line profiles if the broadening is assumed to be mainly caused by long-range interactions with ions and electrons.

3. A Model for the Trajectories

It is usually assumed that during the time of interaction the perturbers move in a straight line relative to the radiating atom, with constant velocity. If v and ρ are the velocity and distance of closest approach of the perturber, then the interaction distance is given by

$$r^2(t) = v^2t^2 + \rho^2 , \tag{3-3.1}$$

where time is measured from the time of closest approach. Consider interactions $H_1(t)$ of the type

$$H_1(t) = \frac{A_n}{r^n(t)} = \frac{A_n}{(v^2t^2 + \rho^2)^{n/2}} . \tag{3-3.2}$$

The time at which $H_1(t)$ is half its maximum value is found from

$$\frac{H_1(0)}{2} = \frac{A_n}{2\rho^n} = \frac{A_n}{(v^2t^2_{1/2} + \rho^2)^{n/2}} , \tag{3-3.3}$$

so that

$$t_{1/2} = \pm (2^{2/n} - 1)^{1/2} \frac{\rho}{v} \sim \pm \frac{\rho}{v} . \tag{3-3.4}$$

The duration τ_d of the collision is of the order of the width of $H_1(t)$ at half its maximum value

$$\tau_d \sim 2t_{1/2} \sim \frac{2\rho}{v} . \tag{3-3.5}$$

The characteristic time τ_d will appear frequently in later arguments and is simply the time during which the principal contribution to the perturbation by a passing particle (e.g., ion or electron) takes place.

4. The Stark Effect in a Homogeneous Electric Field

For sufficiently distant collisions the electric field due to an ion or electron is nearly homogeneous over the radiating atom. If the Bohr radius n^2a_o is taken to be a measure of the linear size of the radiating atom, then the field is essentially homogeneous if the interaction distance,

r, is much greater than n^2a_o

$$r \gg n^2a_o = 4.8\ \text{Å}\ H_\alpha \quad (n=3)$$

(3-4.1)
$$= 8.4\ \text{Å}\ H_\beta \quad (n=4)$$
$$= 13\ \text{Å}\ H_\gamma \quad (n=5)\ .$$

Since most of the interactions take place with $r \gtrsim 100$ Å for the electron densities with which we are concerned here, the effect of inhomogeneous fields is probably not too important. This is confirmed by more quantitative considerations due to Margenau and Meyerott[33] and Spitzer.[9]

Before embarking upon a discussion of the line broadening theory we will first review briefly the theory of the Stark effect in a homogeneous electric field. The theory is, of course, basically different for degenerate systems (hydrogen) and for nondegenerate systems. It is included here because it serves as the foundation for later calculations and discussion.

5. The First-Order Stark Effect in Hydrogen

Consider now a hydrogen atom in an external electric field of strength F in the z direction. The potential energy due to this field is -eFz. The total Hamiltonian is, therefore,

(3-5.1)
$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} - eFz\ .$$

Schrödinger[34] and Epstein[35] have shown that the Schrödinger equation with this Hamiltonian is separable in parabolic coordinates and that $\langle eFz \rangle$ is a diagonal matrix in this representation. The calculation of the Stark shift in the energy levels is then reduced to a simple calculation of the z matrix.

*The following presentation follows that of Condon and Shortley, pages 398-399, Ref. 36.

The Schrödinger equation,

$$H\psi = E\psi \,, \tag{3-5.2}$$

with the Hamiltonian (3-5.1) and the following well-known change variables

$$\begin{aligned} x &= \sqrt{\xi_1 \xi_2}\ \mathrm{Cos}\ \phi \\ y &= \sqrt{\xi_1 \xi_2}\ \mathrm{Sin}\ \phi \\ z &= \tfrac{1}{2}(\xi_1 - \xi_2) \\ \psi &= F_1(\xi_1) F_2(\xi_2)\ \Phi(\phi) \,, \end{aligned} \tag{3-5.3}$$

reduces to the following:

$$\Phi = \frac{e^{im\phi}}{\sqrt{2\pi}} \tag{3-5.4}$$

and

$$\frac{\partial}{\partial \xi_i}\left(\xi_i \frac{\partial F_i}{\partial \xi_i}\right) = -\frac{\mu}{2\hbar^2}\left[E\xi_i + 2e^2 \beta_i - \frac{m\hbar^2}{2\mu\xi_i} + \frac{1}{2} eF\xi_i^2 \right] F_i \tag{3-5.5}$$

where $i = 1,2$.

If we let $\eta_i = \xi_i / n a_o$, where a_o is the first Bohr radius and n is the principal quantum number, then for the electric field strength $F = 0$, equation (3-5.5) can be solved in terms of Laguerre polynomials in the usual way. The solution is

$$F_i(\xi_i) = \eta_i^{\frac{|m|}{2}} e^{-\frac{\eta_i}{2}} L^{|m|}_{k_i}(\eta_i) \,, \tag{3-5.6}$$

where k_1 and k_2 are the parabolic quantum numbers which satisfy the relations

$$n = k_1 + k_2 + |m| + 1 \,; \quad \beta_i = \frac{k_i + \frac{1}{2}|m| + \frac{1}{2}}{n} \,. \tag{3-5.7}$$

Finally, with the correct normalization, the wavefunction which characterizes the state n, k_1, m is

$$\psi_{nk_1m} = \left(\frac{2k_1!\ k_2!}{a_o^3\, n^4\, [(k_1 + |m|)!\ (k_2 + |m|)!]^3}\right)^{1/2} \cdot$$

$$\cdot\ F_1(\eta_1)\ F_2(\eta_2)\ \frac{e^{im\phi}}{\sqrt{2\pi}} \,. \tag{3-5.8}$$

The first-order change in the energy levels of a hydrogen atom due to the electric field can now be calculated using the properties of the Laguerre polynomials:

$$(3\text{-}5.9) \qquad \Delta E = -eF < nk_1m|z|nk_1m > = \frac{3}{2} n (k_1 - k_2) ea_oF \ .$$

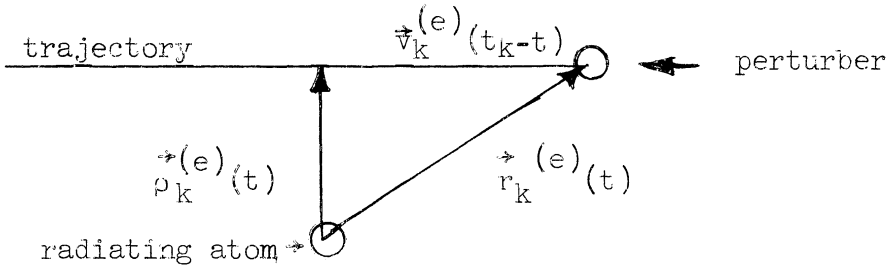
In the classical path approximation the field strength F at a particular time depends on the instantaneous configuration of the assembly of ions and electrons, namely,

$$(3\text{-}5.10) \qquad \vec{F} = \sum_k (\vec{F}_e)_k + \sum_j (\vec{F}_i)_j \ ,$$

where $(\vec{F}_i)_j$ and $(\vec{F}_e)_k$ are the Coulomb fields of the j^{th} ion and k^{th} electron at the radiating atom.

$$(3\text{-}5.11) \qquad (\vec{F}_i)_j = e \vec{r}_j^{(i)}/[r_j^{(i)}]^3 \ , \ (\vec{F}_e)_k = -e\vec{r}_k^{(e)}/[r_k^{(e)}]^3 \ .$$

Because of the time-dependent nature of the interaction distance, these fields are a function of time



so that

$$\vec{r}_k^{(e)}(t) = \vec{\rho}_k^{(e)} + \vec{v}_k^{(e)} (t - t_k)$$

$$\left|\vec{r}_k^{(e)}\right|^3 = [\left|\vec{\rho}_i^{(e)}\right|^2 + \left|\vec{v}_i^{(e)}\right|^2 (t - t_k)^2]^{3/2}$$

$$(3\text{-}5.12) \qquad \vec{\rho}_k^{(e)} \cdot \vec{v}_k^{(e)} = 0 \ .$$

With (3-5.12) we have

$$(3\text{-}5.13) \qquad (\vec{F}_e)_k = \frac{\vec{\rho}_k^{(e)} + \vec{v}_k^{(e)} (t - t_k)}{\{[\rho_k^e]^2 + [v_k^e (t - t_k)]^2\}^{3/2}}$$

and a similar expression for the individual ion fields. Substitution of (3-5.13) into the expression (3-5.10) for the total instantaneous field $\vec{F}$ is seen to have a very complicated time dependence. However, because

of the relatively high and low velocities of the electrons and ions, respectively, it is possible to approximate the interaction Hamiltonian considerably for certain ranges of temperature and density. These approximations will be discussed at length in connection with our discussion of various approximations to the general theory of spectral line broadening in the classical path approximation.

6. Second-Order Stark Effect for Nondegenerate Systems

If the electric field is in the z direction and μ_z is the z component of the atomic electric moment, then the appropriate Hamiltonian is

$$H = H_0 - \mu_z F , \tag{3-6.1}$$

where H_0 is the Hamiltonian for the unperturbed atom. Now for nondegenerate (nonhydrogenic) states having definite parity, the diagonal matrix elements of μ_z are zero since μ_z has odd parity.* The shift of the unperturbed energy levels must then be calculated by second-order perturbation theory and is given by the well-known formula

$$\Delta E = F^2 \sum_{n'\ell'm'}^{E_{n\ell m} \pm E_{n'\ell'm'}} \frac{\langle n\ell m \,|\mu_z|\, n'\ell'm' \rangle \langle n'\ell'm' \,|\mu_z|\, n\ell m \rangle}{E_{n\ell m} - E_{n'\ell'm'}} , \tag{3-6.2}$$

where the $E_{n\ell m}$ are the unperturbed eigenvalues of the unperturbed Hamiltonian, H_0. The above expression defines the polarizability α of the atom, which may be calculated if one has sufficient knowledge of the energy levels and wavefunctions of the unperturbed atom. In the classical path approximation α is left as a phenomenological parameter in the theory. Fortunately, however, a great number of experimental Stark effect data are available for many spectral lines from which α may be determined empirically. These remarks apply only for weak electric fields that do not cause the normally

*See, for example, Condon and Shortley, page 410, Ref. 36.

unperturbed, nondegenerate levels of interest to overlap.

7. Quantum Mechanical Basis of the Classical Path Approximation

The intensity distribution $I(\omega)$ (energy radiated per second) of dipole radiation from a classical charge distribution with a time-dependent dipole moment $\mu(t)$ is proportional to the absolute value squared of the Fourier transform of the dipole moment.*

$$(3\text{-}7.1) \quad I(\omega) = \lim_{T\to\infty} \frac{2\omega^4}{3\pi c^3} \frac{1}{T} \left| \int_0^T dt \mu(t) e^{-i\omega t} \right|^2 .$$

The formal quantum theory can be developed in a variety of ways. According to the correspondence principle, the dipole moment $\mu(t)$ is taken to be a quantum mechanical operator. The intensity distribution is found by taking matrix elements of this operator between the initial and final states involved in the radiative transitions. The initial states must, of course, be weighted with appropriate weighting factors (i.e., the usual Boltzmann factors for a system in thermal equilibrium). Anderson[14] has shown that either correspondence-principle arguments** or a quantum theory for spontaneous radiation leads to the same quantum mechanical generalization of the classical formula (3-7.1). Bloom and Margenau[13] also obtained a similar result by considering absorption processes according to semi-classical radiation theory. Since these results form the starting point for the theory presented in this dissertation, the derivation of Bloom and Margenau is given in Appendix A.

The results of Appendix A are summarized in the remainder of this section. The intensity distribution is found by calculating the proba-

*See, for example, Ref. 37, pp. 125, 193.

**Following the ideas of Klein (Ref. 38) and Pauli (Ref. 39).

bility of a radiative transition between states of a radiating molecule or atom perturbed by interactions with neighboring particles (molecules, atoms, ions, or electrons), as well as by a thermal radiation field. Standard time-dependent perturbation theory is used throughout. If H_o is the Hamiltonian of the unperturbed atom or molecule and $H_1(t)$ is the Hamiltonian which describes the interaction of the radiator with the assembly of perturbers, then there is a set of wavefunctions $\psi_n(t)$ which describe the time development of the perturbed molecule as it collides with the perturbers. The $\psi_n(t)$ satisfy the Schrödinger equation

$$(3\text{-}7.2) \qquad i\hbar\dot{\psi}_n(t) = [H_o + H_1(t)]\psi_n(t) \ .$$

$H_1(t)$ contains explicitly the coordinates of all the particles in the gas. In terms of the wavefunctions $\psi_n(t)$, it is shown in Appendix A that the intensity distribution for dipole radiation is given by the expression

$$I(\omega) = \frac{2\omega^4}{3\pi c^3}\frac{1}{\left(\exp\frac{\hbar\omega}{kT}-1\right)}\left\{\sum_m [\rho_m(0) - \rho_n(0)]\lim_{T\to\infty}\frac{1}{T}\left|\int_0^T dt\mu^c_{nm}(t)e^{-i\omega t}\right|^2\right.$$

$$(3\text{-}7.3) \qquad \left. + \left|\int_0^T dt\mu^c_{nm}(t)\, e^{+i\omega t}\right|^2\right\}_{\text{Avg}} \ ,$$

Avg ≡ average over collisions

where $\mu^c_{nm}(t)$ is a dipole matrix element defined by $[\psi_n(t),\mu\psi_m(t)]$, and $\rho_m(0)$ and $\rho_n(0)$ are Boltzmann factors for states of the radiator having unperturbed energies E^o_m and E^o_n, respectively. The term containing $\rho_m(0)$ in the above sum involves transitions from the states m→n and serves to populate the state n. The second term involves transitions n→m and serves to depopulate the state n. If E_m is greater than E_n, then the m→n transitions correspond to induced emission while the n→m transitions correspond to induced absorption. If $E_n > E_m$, then the opposite is true. The sum over all states m and n therefore includes all processes which involve

induced absorption and emission. Spontaneous emission is, of course, not included since we have not considered the interaction of the radiating system with the electromagnetic vacuum. It can be shown easily that if $E_n^o > E_m^o$, then the term in (3-7.3) containing $(-i\omega t)$ produces resonance while the term with $(+i\omega t)$ is nonresonant and can be dropped in comparison to the resonant term. In the microwave region the nonresonant term is sometimes important but will not concern us here for our considerations of the optical region of the spectrum. The expression (3-7.3) is to be compared with the classical formula (3-7.1), which has the same form. The averaging process denoted by the subscript Avg in (3-7.3) means that one must average over the positions of the perturbing particles since this expression was derived with a definite configuration of perturbers in mind [a definite time-dependent perturbation $H_1(t)$]. The configuration average will be dealt with in detail in subsequent discussions.

8. The Principle of Detailed Balance

For an atomic or molecular system in thermal equilibrium with a radiation field, the energy emitted and absorbed by the matter is related by Kirchoff's law. This law is employed directly in the theory of radiative transfer in stellar atmospheres, for example, to relate the coefficients of emission and absorption when one or the other is calculated theoretically. However, it is known* that the line broadening theory under discussion here apparently does not satisfy the principle of detailed balancing at individual frequencies. It is of some importance to reconcile this difficulty because the application of the semiclassical radiation theory for induced absorption and emission or the spontaneous emission theory of Anderson[14] lead to nontrivial numerical discrepancies in the calculation of the shape of

*See, for example, Bloom and Margenau, Ref. 13.

highly broadened hydrogen lines. The difficulty seems to be connected with the choice of the Boltzmann factor, $\rho_m(0)$ and $\rho_n(0)$, in the intensity distribution (3-7.3). In this section it will be demonstrated that the Boltzmann distribution involves $(E_n^o + \hbar\Delta\omega_n)$ instead of the unperturbed energies E_n^o and that this leads to detailed balance. The quantity $\hbar\Delta\omega_n$ is the perturbation energy of the state n at the initial time t = 0. The proof is restricted to the "static" limit* where the perturbers move so slowly that the perturber configuration does not change appreciably during times of the order $(\Delta\omega_n)^{-1}$.

Van Vleck and Margenau[40] showed that the frequency distribution in the spectral lines of a classical harmonic oscillator and a Debye rotator are the same in absorption and spontaneous emission if the radiation density obeys the Rayleigh-Jeans law. These calculations were restricted to the strong collision theory where each collision is assumed to interrupt the radiation process completely (i.e., destroy all phase relationships). It was also assumed that the time duration of each collision is infinitely short.

Let us consider here an assembly of hydrogen atoms in thermal equilibrium with a Planck radiation field. Suppose that the broadening of the hydrogen Balmer lines is due to the presence of ions only (the electron broadening will require another argument). It is now assumed that the ions can be treated as if they were stationary so that the instantaneous perturbation of the hydrogen atoms can be taken to be time independent. Let the time-independent perturbation of the state n and m be $\Delta\omega_n$ and $\Delta\omega_m$ measured in units of circular frequency. The perturbation energy, of course, depends on the instantaneous configuration of the stationary

*See Section 12 of this chapter for a more detailed discussion of the static or statistical limit of the theory.

ions. Using the results of Section 12, the statistical (static) limit to the theory reduces to the average of a delta function

$$(3\text{-}8.1)\quad \lim_{T\to\infty}\frac{1}{T}\left|\int_{t_o=0}^{T} dt\mu^{c}_{nm}(t)e^{-i\omega t}\right|^2_{Avg} = |\mu_{nm}(0)|^2\,[\delta(\omega-\omega^{o}_{nm}-\Delta\omega_n+\Delta\omega_m)]_{Avg},$$

where ω^{o}_{nm} is the unperturbed frequency corresponding to the transition $n\to m$ and $\hbar\Delta\omega_n$ is the perturbation energy of the state n. Since in the static limit the perturbers do not move during the times of interest, the instantaneous energy at the initial time $t_o=0$ is taken to be constant. The density matrix* at $t_o=0$ therefore involves the total energy, including the perturbation energy, and is given by

$$(3\text{-}8.2)\quad \overline{A^{*}_{m}(0)A_{n}(0)} = \rho_n(0)\,\delta_{mn} = \frac{e^{-(E^{o}_{n}+\hbar\Delta\omega_n)/kT}}{Z(T)}\,\delta_{mn},$$

where Z(t) is the sum over states. It will now be shown that with these Boltzmann factors one obtains detailed balance at all frequencies.

With (3-8.2) the intensity distribution (3-7.3) becomes in the static limit

$$(3\text{-}8.3)\quad I(\omega) = \frac{2}{3}\frac{\omega^4}{\pi c^3}\frac{|\mu_{nm}(0)|^2}{\left(\exp\frac{\hbar\omega}{kT}-1\right)}\left[\sum_m \frac{e^{-\frac{(E^{o}_{m}+\hbar\Delta\omega_m)}{kT}}-e^{-\frac{(E^{o}_{n}+\hbar\Delta\omega_n)}{kT}}}{Z(T)}\cdot\delta(\omega-\omega^{o}_{nm}-\Delta\omega_n+\Delta\omega_m)\right]_{Avg}.$$

Anderson's theory[14] for spontaneous emission yields the following result for the intensity $I_s(\omega)$ in the static limit:

$$(3\text{-}8.4)\quad I_s(\omega) = \frac{2}{3}\frac{\omega^4|\mu_{nm}(0)|^2}{\pi c^3}\sum_m\left[\rho_m(0)\delta(\omega-\omega^{o}_{nm}-\Delta\omega_n+\Delta\omega_m)\right]_{Avg}.$$

Subtracting the two expressions for $I(\omega)$ and $I_s(\omega)$ yields

*See Appendix A.

$$\frac{3\pi c^3 |\mu_{nm}(0)|^{-2}}{2\omega^4} [I(\omega) - I_s(\omega)] = \left\{ \left[\sum_m \frac{e^{-\frac{[E_m^o - E_n^o - \hbar(\Delta\omega_m - \Delta\omega_n)]}{kT}}}{(e^{\hbar\omega/kT} - 1)} - 1 \right] \cdot \right.$$

(3-8.5)

$$\left. \cdot \frac{e^{-(E_m^o + \hbar\Delta\omega_m)/kT}}{Z(T)} \cdot \delta[\omega - (\omega_{nm}^o + \Delta\omega_n - \Delta\omega_m)] \right\}_{Avg} .$$

Now since the delta function is nonzero only for $\omega = \omega_{nm}^o + \Delta\omega_n - \Delta\omega_m$ where $\hbar\omega_{nm}^o = E_n^o - E_m^o$, one observes that the right-hand side of the above expression is identically zero. Therefore, the spontaneous emission just balances the induced absorption and emission.

For very wide hydrogen lines the correction to the Boltzmann distribution due to the static ion field can lead to a measurable asymmetry in the line profile. For an emission line, the ratio of the Boltzmann factor corresponding to the red and blue wing is exp - $(2\hbar\Delta\omega_n/kT)$. For T = 10,000°K and $\Delta\omega_n = 5\times10^{13}$ (50Å from the line center), the ratio of the red to blue intensity due to the corrected Boltzmann factor is

$$e^{-(2\hbar\Delta\omega_n)/kT} \sim 1.1 ,$$

so that the asymmetry is about ten percent. For wider lines asymmetry is correspondingly greater, i.e., for lines 200Å wide, such as are observed in white dwarf stars and in the shock tube, the asymmetry is about 17 percent due to this cause. The existing experimental data are not accurate enough to verify these conclusions, although the shock tube is a promising instrument for the investigation of asymmetries in the Balmer lines.

Further work is needed to generalize this discussion to the case of time-dependent perturbations. It is not clear at the present time what one should take for the density matrix $\rho_n(0)$ at the initial time t = 0. For narrow lines, however, one may safely assume that $\rho_n(0)$ is very nearly the Boltzmann factor corresponding to the unperturbed energies, although the theoretical situation is not completely satisfactory. The difficulties

are closely related to the problem encountered in deriving a statistical transport equation from quantum mechanical perturbation theory, where it is usually assumed that at some initial time the density matrix is diagonal in the unperturbed energy. Although this problem has been dealt with extensively in connection with transport theory, it has been largely ignored in the theory of spectral line broadening.

9. Evaluation of $\mu^c_{nm}(t)$ by Perturbation Theory

Let us consider the broadening of a spectral line originating from a transition between an initial degenerate state i and a final degenerate state f. In hydrogen the degeneracy is $2n^2$, where n is the principal quantum number. For nonhydrogenic levels of other atoms there is also a $(2J+1)$-fold spatial degeneracy in general. The exact calculation of the line broadening would involve the solution of a Schrödinger equation with a time-dependent perturbation due to the entire assembly of fast-moving electrons and slow-moving ions. (We will amplify later the exact meaning of fast and slow.) It would then be necessary to calculate the time-dependent dipole matrix $\mu^c_{nm}(t)$ with the wavefunctions obtained from the appropriate Schrödinger equation. Finally, one would have to substitute this matrix into the formula for the intensity (3-7.3), perform a statistical average over all configurations of the ions and electrons, and finally do the resulting integrals. The approach to the problem as outlined above is prohibitively difficult, so further approximations are required to obtain quantitative results.

In the following discussion, for convenience we drop a factor $4\omega^4[3c^3(\exp \hbar\omega/kT-1)]^{-1}$ in the expression (3-7.3) for the intensity distribution and focus our attention on the term

$$(3\text{-}9.1)\quad \sum_m \rho_m(0) I_{mn}(\omega) = \sum_m \frac{\rho_m(0)}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_0^T dt\ \mu^c_{nm}(t)\ e^{-i\omega t} \right|^2_{\text{Avg}} ;\ E^o_n > E^o_m \ .$$

Induced absorption from all states m which serve to populate the state n are taken into account in the above sum since it refers to transitions for which $E^o_n > E^o_m$ and since initially the state m is occupied. The term $\rho_m(0)$ is the appropriate Boltzmann factor. The above expression defines the quantity $I_{mn}(\omega)$, which is not to be confused with the total intensity $I(\omega)$ in (3-7.3). For simplicity we will refer to $I_{mn}(\omega)$ as the absorption coefficient in the following sections.

Let us now consider a group of spectral lines arising from transitions between an initial state i with substates α and a final state f with substates $\underline{a}$. In the remainder of this work Greek letters refer to substates of the initial state i and Roman letters to substates of the final state f. In (3-9.1) the index $n \to (a,f)$ and $m \to (\alpha,i)$. Summing over all transitions, the absorption coefficient can now be written as a sum over the degenerate substates of i and f

$$(3\text{-}9.2)\quad I_{if}(\omega) = \sum_{\alpha,a} \frac{\rho_a(0)}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_0^T dt\ e^{-i\omega t} (\chi^f_a, \mu \chi^i_\alpha) \right|^2_{\text{Avg}} = \sum_{\alpha a} \rho_\alpha(0)\ I_{a\alpha}(\omega) \ .$$

The expression $\chi^f_a(t)$ describes the time development of a state function which at $t = 0$ reduces to ϕ^f_a, the wavefunction corresponding to the energy E^o_{af} of the $\underline{a}$ substate of the unperturbed state f. These time-dependent wavefunctions satisfy the time-dependent Schrödinger equation (3-7.2). In the following analysis it is assumed that the time-dependent perturbation does not cause transitions between the states i and f. In the case of hydrogen line broadening this assumption means that collision-induced transitions between states of different principal quantum number are

neglected. This is a fundamental limitation of the classical path theory. The energies involved in the collision-induced transitions must be small compared to the kinetic energy of the perturbing particles so that the perturber velocity is not changed appreciably during a collision. A more exact quantum mechanical theory would be required to treat inelastic collisions where the energy changes are large.

It is now convenient* to expand the wavefunctions $\chi_a^f(t)$ and $\chi_\alpha^i(t)$ in terms of the finite orthonormal set of functions $\phi_a^f(t)$ and $\phi_\alpha^i(t)$ which satisfy the instantaneous Schrödinger equation

$$(3\text{-}9.3) \qquad [H_o + H_1(t)] \begin{Bmatrix} \phi_\alpha^i(t) \\ \phi_a^f(t) \end{Bmatrix} = \begin{Bmatrix} E_\alpha^i(t)\ \phi_\alpha^i(t) \\ E_a^f(t)\ \phi_a^f(t) \end{Bmatrix} ,$$

where the time is taken to be a parameter in the stationary Schrödinger equation. The set of functions $\phi_\alpha^i(t)$ and $\phi_a^f(t)$ is chosen to be the unperturbed set ϕ_α^i and ϕ_a^f at $t = 0$. This implies that at some initial time the time-dependent perturbation $H_1(t)$ is effectively zero. We have seen already in our discussion of the principle of detailed balance (Section III.8) that taking $H_1(t)$ to be zero at the initial time is incorrect in the "statistical limit" where $H_1(t)$ is a constant for the times of interest in the Fourier integral expression for the intensity. However, it was also shown that the error introduced was small for lines that are narrow compared to the unperturbed energy difference $E_\alpha(0)-E_a(0)$. For perturbations that vary rapidly in time (e.g., fast electron collisions) one must average somehow over the different possible initial conditions in a more precise theory. Taking $H_1(t)$ to be zero at $t = 0$ avoids these difficulties which are inherent in time-dependent perturbation theories

*See, for example, L. I. Schiff, Quantum Mechanics, p. 208, McGraw-Hill (1949).

where the perturbation is never zero; e.g., in a gas where there are long-range interactions so that a radiating atom is never isolated. For narrow lines, however, the assumption that $H_1(0)=0$ probably does not lead to serious errors.

Dropping the i and f superscripts on the wavefunctions and remembering that the Greek and Roman letters are associated with the substates i and f, respectively, we can now write down the expansions for ψ_α and ψ_a:

$$\psi_\alpha(t) = \sum_\beta C_{\beta\alpha}(t)\, \phi_\beta(t)\, e^{-\frac{i}{\hbar}\int_o^t E_\beta(t')dt'}$$

$$\psi_a(t) = \sum_b C_{ba}(t)\, \phi_b(t)\, e^{-\frac{i}{\hbar}\int_o^t E_b(t')dt'} \qquad (3\text{-}9.4)$$

Substitution of (3-9.4) into the Schrödinger equation (3-7.2) and using (3-9.3) yields an expression for the expansion coefficients:

$$\dot{C}_{ba}(t) = -\sum_d C_{da}(\phi_b,\dot{\phi}_d)\, e^{-\frac{i}{\hbar}\int_o^t E_{db}(t')dt'}$$

$$\dot{C}_{\beta\alpha}(t) = -\sum_\gamma C_{\gamma\alpha}(\phi_\beta,\dot{\phi}_\gamma)\, e^{-\frac{i}{\hbar}\int_o^t E_{\gamma\beta}(t')dt'} \qquad (3\text{-}9.5)$$

where $E_{db}(t) = E_d(t) - E_b(t)$ and $E_{\gamma\beta}(t) = E_\gamma(t) - E_\beta(t)$. Now in the usual fashion one can find an alternative form for the matrix $(\phi_\beta,\dot{\phi}_\alpha)$ by differentiating (3-9.3) and multiplying by ϕ_β:

$$(\phi_\beta, \dot{H}\phi_\alpha) + (\phi_\beta, H\dot{\phi}_\alpha) = (\phi_\beta, \dot{E}_\alpha\phi_\alpha) + (\phi_\beta, E_\alpha\dot{\phi}_\alpha);\ H \equiv H_o + H_1(t). \qquad (3\text{-}9.6)$$

For $\beta=\alpha$, $(\phi_\beta, \dot{E}_\alpha\phi_\alpha) = 0$ because of the orthogonality of the wavefunctions; also, because of tne Hermitian character of H,

$$(3\text{-}9.7) \qquad (\phi_\beta, \dot{H}\dot{\phi}_\alpha) = (H\phi_\beta, \ddot{\phi}_\alpha) = E_\beta(\phi_\beta, \phi_\alpha) ,$$

so that (3-9.6) reduces to

$$(3\text{-}9.8) \qquad (\phi_\beta, \dot{\phi}_\alpha) = \frac{(\phi_\beta, \dot{H}\phi_\alpha)}{E_\alpha - E_\beta} = \frac{\dot{H}_{\beta\alpha}}{E_{\alpha\beta}} \quad \beta \neq \alpha .$$

Substitution of this identity into (3-9.5) gives

$$(3\text{-}9.9) \qquad \dot{C}_{\beta\alpha} = -\sum_\gamma{}' C_{\gamma\alpha} \frac{\dot{H}_{\beta\gamma}}{E_{\gamma\beta}} e^{-\frac{i}{\hbar}\int_0^t E_{\gamma\beta}(t')dt'} - C_{\beta\alpha}(\phi_\beta, \ddot{\phi}_\beta)$$

(with the usual notation $\sum_{\gamma\neq\alpha} \equiv \sum_\gamma{}'$) and similarly for $\dot{C}_{ba}(t)$.

The set of equations (3-9.9) form a finite set of coupled linear differential equations. These equations have a simple solution in two extreme cases: (1) if the perturbing field is essentially static, then $\dot{H}(t) \simeq 0$ and the nondiagonal elements of $C_{\beta\alpha}(t)$ vanish; (2) for long-range interactions (large impact parameters) it is sometimes the case that the $C_{\beta\alpha}(t) \ll 1$; then only the term $C_{\alpha\alpha}(t) \sim C_{\alpha\alpha}(0) = 1$ contributes to the right-hand side of equation (3-9.9) for the expansion coefficients $C_{\beta\alpha}(t)$. If the nondiagonal elements, $C_{\beta\alpha}(t)$; $\beta\neq\alpha$, are neglected completely, then one is dealing with the usual adiabatic theory of spectral line broadening. It is shown in Sections 11 and 12 of this chapter that this approximation is valid for hydrogen lines broadened by slow-moving ions. In Chapter V, however, it will be demonstrated that the neglect of collision-induced transitions by plasma electrons leads to serious errors. In order to take the electron broadening into account properly, the time-dependent dipole matrix $\mu^c_{a\alpha}(t)$ is calculated in this section up to first order in $C_{\beta\alpha}(t)$ [or equivalently to first order in $H_1(t)$]. It turns out that this "weak collision" theory is adequate for our problem because of the long-range nature of the Coulomb potential.

With the weak collision approximation $[C_{\alpha\alpha}(t) \sim C_{\alpha\alpha}(0) = 1; |C_{\beta\alpha}(t)| \ll 1]$ the amplitude equation (3-9.9) becomes

$$\dot{C}_{\beta\alpha}(t) = -\frac{[\dot{H}_1(t)]_{\beta\alpha}}{E_{\alpha\beta}(t)} e^{-\frac{i}{\hbar}\int_0^t E_{\alpha\beta}(t')dt'} \tag{3-9.10}$$

since $\dot{H}_{\beta\alpha}(t) \equiv [\dot{H}_0 + \dot{H}_1(t)]_{\beta\alpha} = [\dot{H}_1(t)]_{\beta\alpha}$.

Integrating (3-9.10) directly yields

$$C_{\beta\alpha}(t) = -\int_0^t \frac{[\dot{H}_1(t'')]_{\beta\alpha}}{E_{\alpha\beta}(t'')} e^{-\frac{i}{\hbar}\int_0^{t''} E_{\alpha\beta}(t')dt'} dt'' \tag{3-9.11}$$

If the perturbation is due to a finite number, k, of passing electrons whose time of closest approach t_k is large compared to τ_d (where τ_d again is the collision duration discussed in Section 5), then $H_1(0) \sim 0$. Making use of this, together with the relation, $H_1(\infty)=0$, a partial integration yields

$$\lim_{t \to \infty} C_{\beta\alpha}(t) = -\frac{i}{\hbar}\int_0^t [H_1(t'')]_{\beta\alpha} e^{-\frac{i}{\hbar}\int_0^{t''} E_{\alpha\beta}(t')dt'} dt'' \tag{3-9.12}$$

The wavefunctions $\psi_\alpha(t)$ and $\psi_a(t)$ (equation 3-9.4) can now be expressed in terms of these expansion coefficients:

$$\psi_\alpha = \phi_\alpha(t)\, e^{-\frac{i}{\hbar}\int_0^t E_\alpha dt'} + \sum_\beta{}' C_{\beta\alpha}(t)\phi_\beta(t)\, e^{-\frac{i}{\hbar}\int_0^t E_\beta dt'}$$

$$\psi_a = \phi_a(t)\, e^{-\frac{i}{\hbar}\int_0^t E_a dt'} + \sum_b{}' C_{ba}(t)\phi_b(t)\, e^{-\frac{i}{\hbar}\int_0^t E_b dt'} \tag{3-9.13}$$

$$E_\alpha \equiv E_\alpha(t)\ ,\ \psi_\alpha \equiv \psi_\alpha(t)\ ,$$

where to first order, $C_{\alpha\alpha}(t) \cong C_{aa}(t) \cong 1$.

With these wavefunctions the dipole matrix $\mu^c_{a\alpha}(t)$ becomes

$$(\chi_a,\mu\chi_\alpha) \equiv \mu^c_{a\alpha}(t) = (\phi_a,\mu\phi_\alpha)\, e^{-\frac{i}{\hbar}\int_0^t (E_\alpha - E_a)dt'}$$

$$+ \sum_b{}' (\phi_b,\mu\phi_\alpha)\, C^*_{ba}\, e^{-\frac{i}{\hbar}\int_0^t (E_\alpha - E_b)\, dt'}$$

(3-9.14)

$$+ \sum_\beta{}' (\phi_a,\mu\phi_\beta)\, C_{\beta\alpha}\, e^{-\frac{i}{\hbar}\int_0^t (E_\beta - E_a)dt'}$$

$$+ \sum_{b,\beta} (\phi_\beta,\mu\phi_b) C_{\beta\alpha}\, C^*_{ba}\, e^{-\frac{i}{\hbar}\int_0^t (E_\beta - E_b)dt'} \quad .$$

Consistent with our perturbation treatment it is assumed that the line strength is given to first order by the unperturbed strengths:

(3-9.15) $$[\phi_a(t),\mu\phi_\alpha(t)] \cong [\phi_a(0),\mu\phi_\alpha(0)] \equiv \mu^o_{a\alpha} \quad .$$

We also drop the last term in (3-9.14) as small compared to terms of order $C_{\beta\alpha}(t)$ and $C_{ba}(t)$. The dipole matrix is now

$$\mu^c_{a\alpha}(t) = \mu^o_{a\alpha}\, e^{-\frac{i}{\hbar}\int_0^t (E_\alpha - E_a)\, dt'}$$

$$+ \sum_b{}' \mu^o_{ba}\, C^*_{ba}(t)\, e^{-\frac{i}{\hbar}\int_0^t (E_\alpha - E_b)dt'}$$

(3-9.16)

$$+ \sum_\beta{}' \mu^o_{a\beta}\, C_{\beta\alpha}(t)\, e^{-\frac{i}{\hbar}\int_0^t (E_\beta - E_a)dt'} \quad .$$

The time-dependent energy is given by

(3-9.17) $$E_\alpha(t) = [\phi_\alpha(t),E_o\phi_\alpha(t)] + [\phi_\alpha(t),H_1(t)\phi_\alpha(t)] \quad .$$

To first order this becomes

(3-9.18) $$E_\alpha(t) = [\phi_\alpha(0),H_o\phi_\alpha(0)] + [\phi_\alpha(0),H_1(t)\phi_\alpha(0)] = E^o_\alpha + [H_1(t)]^o_{\alpha\alpha}$$

or

(3-9.19) $$\omega_\alpha(t) = \omega^o_\alpha + \Delta\omega_\alpha(t)$$

where $\hbar\omega^o_\alpha(t) \equiv E_\alpha(t)$ and $\hbar\Delta\omega_\alpha(t) = [H_1(t)]^o_{\alpha\alpha}$. The expression $[H_1(t)]^o_{\alpha\alpha}$ is simply the time-dependent shift in the position of the state α as a consequence of the perturbation.

Then

$$(3\text{-}9.20) \qquad \frac{i}{\hbar}\int_o^t E_\alpha(t')dt' = \omega_\alpha^o\, t + \int_o^t \Delta\omega_\alpha(t')dt' \quad .$$

For further simplification let us abbreviate the integral on the right side of this last identity,

$$(3\text{-}9.21) \qquad P_{\alpha\alpha}(t) \equiv \int_o^t \Delta\omega_\alpha(t')dt' \quad .$$

Employing these definitions and factoring out $\mu_{a\alpha}^o$ and exp i $(\omega_\alpha^o - \omega_a^o)t$ from (3-9.16), we obtain the following expression for $\mu_{a\alpha}^c(t)$:

$$\mu_{a\alpha}^c(t) = \mu_{\alpha a}^o\, e^{i(\omega_a^o - \omega_\alpha^o)t}\left\{\frac{\mu_{a\alpha}^o}{\mu_{\alpha a}^o}\, e^{-i[P_{\alpha\alpha}(t)-P_{aa}(t)]}\right.$$

$$(3\text{-}9.22) + \sum_b{}' \frac{\mu_{b\alpha}^o}{\mu_{\alpha a}^o}\, C_{ba}^*(t)\, e^{i(\omega_b^o - \omega_a^o)\,t + i\,[P_{bb}(t)-P_{\alpha\alpha}(t)]}$$

$$\left. + \sum_\beta{}' \frac{\mu_{a\beta}^o}{\mu_{\alpha a}^o}\, C_{\beta\alpha}(t)\, e^{i(\omega_\alpha^o - \omega_\beta^o)\,t + i\,[P_{aa}(t)-P_{\beta\beta}(t)]}\right\} \quad .$$

The spectral distribution in the line i → f is related to the absolute value squared of the Fourier transform of $\mu_{a\alpha}^c(t)$ according to (3-7.3). The so-called adiabatic and impact theories of line broadening are contained in this result as special cases.

10. Adiabatic Approximation

In the adiabatic approximation to the theory of line broadening the expansion coefficients $C_{ba}(t)$ and $C_{\beta\alpha}(t)$ are taken to be zero so that the nondiagonal matrix elements of the perturbation Hamiltonian do not enter into the problem. As is well known, this approximation neglects collision-induced transitions and thereby allows a great simplification in the theory. Since the adiabatic theory has been extensively applied by other authors to various line broadening problems and because it contains much of the

essential features of a more accurate classical path theory which takes into account collision-induced transitions, we will discuss this approximation in some detail.

In the expression (3-9.22) for $\mu^{o}_{a\alpha}(t)$ the expansion coefficients $C_{ba}(t)$ and $C_{\beta d}(t)$ are taken to be zero in the adiabatic limit, so that the dipole matrix becomes

$$(3\text{-}10.1) \qquad [\mu^{c}_{a\alpha}(t)]_{Ad} = \mu^{o}_{a\alpha}\, e^{-i\,\omega^{o}_{a\alpha}t - i[P_{\alpha\alpha}(t)-P_{aa}(t)]}$$

where we have put $\omega^{o}_{a} - \omega^{o}_{\alpha} \equiv \omega^{o}_{a\alpha} > 0$. Substitution of this time-dependent matrix into the general expression for the absorption coefficient (3-9.2) yields

$$(3\text{-}10.2) \qquad I_{a\alpha}(\omega) = \lim_{T\to\infty} \frac{|\mu_{a\alpha}|^2}{2\pi} \frac{1}{T} \left| \int_{o}^{T} dt\; e^{-i\Delta\omega^{o}_{a\alpha}t - i[P_{\alpha\alpha}(t)-P_{aa}(t)]} \right|^2_{Avg},$$

where $\Delta\omega^{o}_{a\alpha} \equiv \omega - \omega^{o}_{a\alpha}$. The usual correlation function form of this formula is found by writing $I_{a\alpha}(\omega)$ in the following form:

$$I_{a\alpha}(\omega) = \lim_{T\to\infty} |\mu^{o}_{a\alpha}|^2 \left\{ \int_{o}^{T} dt_2 \int_{o}^{T} dt_1\; e^{i\Delta\omega^{o}_{a\alpha}(t_1-t_2)} \cdot \right.$$

$$(3\text{-}10.3) \qquad \left. \cdot\; e^{-i[P_{\alpha\alpha}(t_1)-P_{\alpha\alpha}(t_2)+P_{aa}(t_1)-P_{aa}(t_1)]} \right\}_{Avg},$$

where $P_{\alpha\alpha}(t_1)-P_{\alpha\alpha}(t_2) = \int_{t_2}^{t_1} \Delta\omega_{\alpha}(t')dt'$; $P_{aa}(t_2)-P_{aa}(t_1) = -\int_{t_2}^{t_1} \Delta\omega_{a}(t')dt'$.

Putting $t_1 - t_2 = \tau$, and integrating over τ, holding t_2 constant, yields

$$(3\text{-}10.4) \qquad I_{a\alpha}(\omega) = \lim_{T\to\infty} \frac{|\mu_{a\alpha}|^2}{2\pi T} \int_{o}^{T} dt_2 \left[\int_{-t_2}^{T-t_2} d\tau\; e^{-i\Delta\omega^{o}_{a\alpha}\tau}\, e^{-i\int_{t_2}^{\tau+t_2}(\Delta\omega_{\alpha}-\Delta\omega_{a})dt'} \right]_{Avg}.$$

Now in a time interval T, the initial and final times do not affect the statistical average for statistically stationary distribution of perturbing

particles. Therefore, in the adiabatic approximation the absorption coefficient is simply

$$(3\text{-}10.5) \qquad I_{a\alpha}(\omega) = \frac{|\mu^{o}_{a\alpha}|^2}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{i\int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt'} \right]_{Avg} .$$

In the static approximation, where the perturbation Hamiltonian is time independent, the phase integral becomes

$$\int_{o}^{t} (\Delta\omega_a - \Delta\omega_\alpha)dt' = (\Delta\omega_a - \Delta\omega_\alpha)t .$$

In this approximation the absorption coefficient (3-10.5) reduces to the average of a delta function over the perturber coordinates (see Section 12 of this chapter for a more detailed discussion):

$$(3\text{-}10\ 6) \qquad I_{a\alpha}(\omega) = |\mu^{o}_{a\alpha}|^2\, \delta \left\{ [\Delta\omega^{o}_{a\alpha} - (\Delta\omega_a - \Delta\omega_\alpha)] \right\}_{Avg} .$$

It can also be shown in general that if $\Delta\omega_a - \Delta\omega_\alpha$ is an even function of time, then

$$\int_{-\infty}^{o} d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{i\int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt'} \right]_{Avg}$$

$$= \int_{o}^{\infty} d\tau\, e^{+i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{-i\int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt'} \right]_{Avg} ,$$

so that (3-10.5) can also be written

$$(3\text{-}10.7) \qquad I_{a\alpha}(\omega) = \frac{|\mu^{o}_{a\alpha}|^2}{\pi} \mathrm{Re} \int_{o}^{\infty} d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{i\int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt'} \right]_{Avg} .$$

The factor π is a normalization constant such that

$$(3\text{-}10.8) \qquad \int_{-\infty}^{\infty} I_{a\alpha}(\omega)\, d\omega = |\mu^{o}_{a\alpha}|^2 .$$

This will be verified in Chapter V.

The integral (3-10.7) can also be simplified considerably if the perturbers move sufficiently fast or slowly. These approximations are commonly referred to as the phase-shift and statistical approximations, respectively. In Sections 12 and 13 of this chapter these two limiting cases will be discussed in some detail and rather simple derivations of their range of validity will be presented. In addition it will be shown that the usual assumption of binary collisions can be removed from the phase-shift theory for scalarly additive perturbations.

11. Average Over Collisions

The phase factor which appears in the adiabatic theory (equation 3-10.8) must now be averaged over all types of collisions. Let us focus our attention on a particular radiating atom perturbed by an assembly of particles (ions, electrons, neutral atoms or molecules) assumed to move on linear trajectories. In particular, take the case of scalarly additive perturbations of the type

$$(3\text{-}11.1) \qquad \Delta\omega_a - \Delta\omega_\alpha = \sum_{jk} N_{jk} \frac{A_{a\alpha}(\sigma_j)}{r_j^n (t-t_k)} = \sum_{jk} \frac{N_{jk} \cdot A_{a\alpha}(\sigma_j)}{[v_k^2(t-t_k)^2 + \rho_j^2]^{n/2}} ,$$

where t_k is the time of closest approach, v_k is the velocity, ρ_j is the impact parameter, and N_{jk} is the number of perturbing particles described by the variables $(\sigma_j, \rho_j, v_k, t_k)$. The proportionality constant $A_{a\alpha}(\sigma_j)$ is taken to be a known parameter for the interaction of interest. It can depend, in general, on other collision parameters denoted by σ_j. For example, when a fast electron interacts with a hydrogen atom, $A_{a\alpha}(\sigma_j)$ has a $\cos\theta_j$ angular dependence, where θ_j is the angle determined by the position vector $\vec{r}_j(t-t_k)$ of the electron and the dipole moment vector of the atom (see Chapter V).

For scalarly additive perturbations of the type (3-11.1), the phase factors to be averaged are

$$(3\text{-}11.2)\qquad \left[e^{i\sum_{jk} N_{jk} P_{na\alpha jk}(\tau)}\right]_{Avg} \equiv \left[e^{i\sum_{jk} N_{jk}\int_0^\tau dt\ \frac{A_{a\alpha}(\sigma_j)}{r_j^n(t-t_k)}}\right]_{Avg} ,$$

where the quantity $P_{na\alpha jk}(\tau)$ has been introduced for simplicity. The index n denotes the power in the $r_j(t-t_k)$ dependence of the interaction, a and α refer to the atomic states in question, and (j,k) refer to collisions described by the variables $(v_k, t_k, \rho_j, \sigma_j)$.

For sufficiently dilute gases it can be assumed that the individual perturbers move essentially independently of one another so that the average phase factor (3-11.2) can be written as a product,

$$(3\text{-}11.3)\qquad \left[e^{i\sum_{jk} N_{jk} P_{na\alpha jk}(\tau)}\right]_{Avg} = \prod_{jk}\left[e^{iN_{jk}P_{na\alpha jk}(\tau)}\right]_{Avg} .$$

The probability that $N_k(v_k)$ of the particles with velocity v_k have a time of closest approach in $(t_k, t_k + \Delta t_k)$ is given by the familiar Poisson distribution for purely random t_k:

$$(3\text{-}11.4)\qquad W_{N_k}(t_k) = \frac{1}{N_k!}\left(\frac{\Delta t_k}{\tau_k}\right)^{N_k} e^{-\frac{\Delta t}{\tau_k}} ,$$

where τ_k is the mean time between collisions with velocities in the range (v_k, v_k+dv_k). If the assembly of perturbers is contained in a spherical box of radius R, then τ_k is given by the kinetic-theory result

$$(3\text{-}11.5)\qquad \frac{1}{\tau_k} = \pi R^2 v_k N_k(v_k)dv_k .$$

$N_k(v_k)dv_k$ is the average number of perturbers per unit volume with velocities in the range (v_k, v_k+dv_k) and is given by the Boltzmann distribution

$$(3\text{-}11.6)\qquad \frac{N_k(v_k)}{N} dv_k = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v_k^2\, e^{-\frac{m}{2}\frac{v_k^2}{kT}} dv_k \equiv W(v_k)dv_k .$$

N is the number of perturbers per cubic centimeter.

The probability that of these $N_k(v_k)$ particles, N_{jk} have ρ_j and σ_j in the range $(\rho_j, \rho_j+\Delta\rho_j)$, $(\sigma_j, \sigma_j+\Delta\sigma_j)$ is given by Bernoulli distribution for randomly distributed variables:

$$W_{N_{jk}}(\sigma_j,\rho_j) = \frac{N_k!}{N_{jk}!}\left(\frac{2\pi\rho_j\Delta\rho_j}{\pi R^2}\,\frac{\Delta\rho_j}{\Sigma}\right)^{N_{jk}} , \tag{3-11.7}$$

where

$$\sum_k \sum_j N_{jk} = \sum_k N_k = N$$

$$\sum_j 2\pi\rho_j\Delta\rho_j = \pi R^2 \tag{3-11.8}$$

$$\sum_j \Delta\sigma_j = \Sigma$$

The element of phase space $(\Delta\sigma_j\Delta\rho_j\Delta t_k)$ can now be taken small enough in the limit so that it can contain but one particle at a time; then $N_{jk} = 0,1$. Weighting each configuration with the probabilities $W_{N_k}(t_k)$ and $W_{N_{jk}}(\rho_j,\sigma_j)$, the average phase factor (3-11.3) can be written

$$\prod_{jk}\left[e^{iN_{jk}P_{na}\alpha_{jk}(\tau)}\right]_{Avg} = \prod_{jk}\sum_{N_{jk}=0}^{1} W_{N_k}(t_k)W_{N_{jk}}(\rho_j\sigma_j)\, e^{iN_{jk}P_{na}\alpha_{jk}(\tau)}$$

$$= \prod_{jk}\sum_{N_{jk}=0}^{1} e^{-\frac{\Delta t_k}{\tau_k}}\,\frac{1}{N_{jk}!}\left(\frac{2\pi\rho_j\Delta\rho_j}{\pi R^2}\,\frac{\Delta\sigma_j}{\Sigma}\,\frac{\Delta t_k}{\tau_k}\right)^{N_{jk}} e^{iN_{jk}P_{na}\alpha_{jk}(\tau)} . \tag{3-11.9}$$

Substitution of (3-11.5) and (3-11.6) into (3-11.9) and summing over $N_{jk}=0,1$ yields*

$$\prod_{jk} e^{-\frac{\Delta t_k}{\tau_k}}\left[1 + 2\pi N v_k\rho_j\Delta\rho_j\,\frac{\Delta\sigma}{\Sigma}\,\Delta t_k\, W(v_k)dv_k\, e\right]^{iP_{na}\alpha_{jk}(\tau)} . \tag{3-11.10}$$

Now since $\lim_{\xi\to 0} e^{\xi} = 1 + \xi$,

*Summing $N_{jk} = 0 \to \infty$ yields identically the same result.

the average phase factor (3-11.10) is

$$\lim_{\Delta\rho_j,\Delta\sigma_j,\Delta t_k\to 0} e^{\sum_{jk}\left[2\pi N v_k \rho_j \Delta\rho_j \frac{\Delta\sigma}{\sum} \Delta t_k\, W(v_k)dv_k\, e^{iP_{na\alpha jk}(\tau)} - \frac{\Delta t_k}{\tau_k}\right]} \quad (3\text{-}11.11)$$

Replacing the sums by integrals over the continuous variables t_k, ρ_j, σ_j, v_k, and letting $R\to\infty$, yields

$$\left[e^{i\int_0^\tau(\Delta\omega_a-\Delta\omega_\alpha)dt}\right]_{Avg} = e^{2\pi N\int_0^\infty W(v_k)v_k dv_k\int_0^\infty \rho_j d\rho_j \int_0^{\sum} \frac{d\sigma_j}{\sum}\int_0^\infty dt_k[e^{iP_{na\alpha jk}(\tau)}-1]} . \quad (3\text{-}11.12)$$

12. Statistical Approximation

The statistical approximation to the adiabatic theory of line broadening has been extensively discussed by many authors.[5-7,9-12,14,41-47] In this section the validity criteria derived by Holstein[47] for the statistical approximation to the adiabatic theory will be obtained in a simple fashion. It will then be demonstrated that in the validity range of the statistical theory collision-induced transitions can also be neglected for degenerate or nearly degenerate systems under certain conditions. The present investigation was carried out because it was not clear to the writer that the Holstein validity criteria should necessarily be the same with degeneracy. It was also of importance to determine how to incorporate the statistical theory for ion broadening into a quantum mechanical theory which also took electron broadening into account.

The phase $P_{na\alpha jk}(\tau)$ due to the passage of the nearest perturber is written

$$P_{na\alpha jk}(\tau) \equiv \int_0^\tau \frac{A_{a\alpha}(\sigma_j)dt}{[(t-t_k)^2 v_k^2 + \rho_j^2]^{n/2}}$$

$$= \frac{A_{a\alpha}(\sigma_j)}{\rho_j^n}\int_0^\tau \frac{dt}{\left\{\left[\frac{v_k(t-t_k)}{\rho_j}\right]^2+1\right\}^{n/2}} . \quad (3\text{-}12.1)$$

Expanding the integrand by the binomial theorem yields

$$P_{na\alpha jk}(\tau) = \frac{A_{a\alpha}(\sigma_j)}{\rho_j^n}\int_0^\tau dt\left[1 - \frac{n}{2}\frac{v_k^2}{\rho_j^2}(t - t_k)^2 + \cdots\right]$$

(3-12.2)

$$= \frac{A_{a\alpha}(\sigma_j)}{\rho_j^n}\tau\left[1 - \frac{nv_k^2}{6\rho^2\tau}[(\tau - t_k)^3 + t_k^3] + \cdots\right] .$$

Now let $\tau - t_k = \Delta\tau$, and for convenience shift the time origin to t_k so that

$$P_{na\alpha jk}(\tau) = \frac{A_{a\alpha}(\sigma_j)}{\rho_j^n}\tau\left[1 - \frac{nv_k^2}{6\rho_j^2}(\Delta\tau)^2 + \cdots\right] . \tag{3-12.3}$$

In the statistical limit it is required that the higher-order terms in (3-12.3) be small compared to unity:

$$\frac{n}{6}\left(\frac{\Delta\tau v_k}{\rho_j}\right)^2 = \frac{2n}{3}\left(\frac{\Delta\tau}{\tau_d}\right) \ll 1, \tag{3-12.4}$$

where

$$\tau_d = 2\rho_j/v_k ,$$

where τ_d is again the duration of the collision. For frequencies determined by $\Delta\omega\Delta\tau \sim 1$, (3-12.4) yields

$$\frac{n}{6}\left(\frac{v_k}{\rho_j\Delta\omega}\right) \ll 1 . \tag{3-12.5}$$

When this inequality is satisfied the time-dependent perturbation can be considered to be static.

The shift in frequency corresponding to the static field is

$$\Delta\omega = \frac{A_{a\alpha}(\sigma_j)}{\rho_j^n} , \tag{3-12.6}$$

so that

$$\rho_j = \left[\frac{A_{a\alpha}(\sigma_j)}{\Delta\omega}\right]^{\frac{1}{n}} . \tag{3-12.7}$$

Substituting this expression into the inequality (3-12.5) yields the Holstein inequality[47]

$$(3\text{-}12.8) \qquad \omega\Delta \gg \left[\frac{v_n}{A_{a\alpha}(\sigma_j)}\right]^{\frac{1}{n-1}} \left(\frac{n}{6}\right)^{n/n-1} .$$

These inequalities also imply that the total phase shift is large compared to unity in the statistical limit. This fact will be important in our discussion of nonadiabatic effects for degenerate systems. To see this, substitute (3-12.6) into the inequality (3-12.5); then

$$(3\text{-}12.9) \qquad \frac{A_{a\alpha}(\sigma_j)}{\rho_j^{n-1} v_k} \left(\frac{6}{n}\right)^{1/2} \gg 1 .$$

The total phase shift per collision is given by

$$(3\text{-}12.10) \quad P_{na\alpha jk}(\infty) = \int_{-\infty}^{\infty} \frac{A_{a\alpha}(\sigma_j)\, dx}{(v_k^2 x^2 + \rho^2)^{1/2}} = \frac{A_{a\alpha}(\sigma_j)}{\rho_j^{n-1} v_k} \int_{-\infty}^{\infty} \frac{d\bar{x}}{(\bar{x}^2 + 1)^{1/2}} .$$

Substitution of $P_{na\alpha jk}(\infty)$ into the inequality (3-12.9) gives

$$(3\text{-}12.11) \qquad P_{na\alpha jk}(\infty) \gg \frac{n}{6} \int_{-\infty}^{\infty} \frac{d\bar{x}}{(\bar{x}^2+1)^{1/2}} \sim 1 .$$

The line profile in the statistical or static limit can now be found from the adiabatic theory (equation 3-10.7) as a special case. According to (3-11.13), the average phase is given by

$$(3\text{-}12.12) \quad \left[e^{i\int_0^\tau (\Delta\omega_a - \Delta\omega_\alpha)dt}\right]_{Avg} = e^{2\pi N \int_0^\infty W(v_k)dv_k \int_0^\infty \rho_j d\rho_j \int_0^{\sum} \frac{d\sigma_j}{\sum} \int_0^\infty v_k dt_k \left[e^{iP_{na\alpha jk}(\tau)} - 1\right]},$$

where, according to (3-11.2),

$$P_{na\alpha jk}(\tau) \equiv \int_0^\tau \frac{A_{a\alpha}(\sigma_j)dt}{[(v_k t_k - v_k t)^2 + \rho_j^2]^{n/2}} .$$

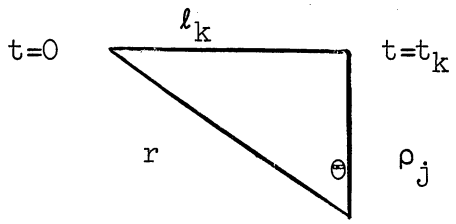
Consider now the integral

$$(3\text{-}12.13)\qquad \int_0^\infty \rho_j d\rho_j \int_0^\infty v_k dt_k \left\{ e^{i\int_0^\tau \frac{A_{a\alpha}(\sigma_j)dt}{[(v_k t_k - v_k t)^2 + \rho_j^2]^{n/2}}} - 1 \right\} .$$

The quantity $v_k t_k \equiv \ell_k$ is the distance traveled by the k^{th} perturber during the time interval $(t=0 \to t_k)$, where t_k is the time of closest approach. Now in the static limit to the adiabatic theory one is concerned with times in the Fourier integral that are much shorter than the duration of a collision. For such short time intervals it has been shown that the perturbation is essentially static. Therefore, the distance $r(t-t_k)$ to the k^{th} perturber given by $r(t-t_k)=[r(t-t_k)]_{t=0}$, the position at the initial time $t=0$. The integral (3-12.13) can therefore be written in the static limit

$$(3\text{-}12.14)\qquad \lim_{v_k \to 0} \int_0^\infty \rho_j d\rho_j \int_0^\infty d\ell_k \left\{ e^{i\int_0^\tau \frac{A_{a\alpha}(\sigma_j)dt}{[(v_k t_k)^2 + \rho_j^2]^{n/2}}} - 1 \right\} .$$

Consider now the diagram



For fixed r (since the perturbers do not move in this approximation) and v_k we have

$$\frac{\ell_k}{r} = \sin\theta \quad , \quad d\ell_k = r\cos\theta\, d\theta$$

$$(3\text{-}12.15)\qquad \lim_{v_k \to 0} \int_0^\infty d\ell_k = \lim_{v_k \to 0} r \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos\theta\, d\theta = \lim_{v_k \to 0} 2r = 2\rho_j .$$

The integral (3-12.14) is now

$$(3\text{-}12.16)\qquad 2\int_0^\infty \rho_j^2\, d\rho_j \left[e^{iA_{a\alpha}(\sigma_j)/\rho_j^n} - 1 \right] .$$

Substituting this expression back into (3-11.13) yields the statistical approximation to the phase factor

$$(3\text{-}12.17)\quad \left[e^{\,i\int_0^\tau (\Delta\omega_a-\Delta\omega_\alpha)dt}\right]_{Avg} = e^{\,4\pi N\int_0^\infty \rho_j d\rho_j \int_0^\Sigma \frac{d\sigma_j}{\Sigma}\left[e^{\frac{iA_{a\alpha}(\sigma_j)\tau}{\rho_j^n}}-1\right]} .$$

The absorption coefficient with (3-12.17) is now

$$(3\text{-}12.18)\quad I_{a\alpha}(\omega) = \frac{|\mu_{a\alpha}|^2}{\pi}\,\mathrm{Re}\int_0^\infty d\tau\; e^{-i\Delta\omega_{a\alpha}\tau + 4\pi N\int_0^\infty \rho_j^2 d\rho_j \int_0^\Sigma \frac{d\sigma_j}{\Sigma}\left[e^{\,i\frac{A_{a\alpha}(\sigma_j)\tau}{\rho^n}}-1\right]}$$

and agrees with the usual form of the statistical theory of Margenau,[42] Holtsmark,[5] Chandrasekhar,[46] et al. The situation when the perturbations add vectorially can be treated by the same methods and will be discussed in detail in subsequent chapters in connection with the theory of hydrogen line broadening by ion fields.

The influence of nonadiabatic transitions can now be investigated in the statistical limit. According to (3-9.11), the expansion coefficients $C_{\beta\alpha}(t)$ are given by

$$C_{\beta\alpha}(t) = \int_0^t dt''\,\frac{[\dot{H}_1(t'')]_{\beta\alpha}}{E_{\beta\alpha}(t'')}\; e^{-\frac{i}{\hbar}\int_0^t E_{\alpha\beta}(t')dt'} ,$$

where $|C_{\beta\alpha}(t)|^2$ is the probability of a transition to the state β if at the beginning of the perturbation the radiating atom is in the state α. Consider again perturbations of the type

$$(3\text{-}12.19)\quad [H_1(t)]_{\alpha\alpha} - H_1(t)_{\beta\beta} = \frac{\hbar\, A_{\alpha\beta}(\sigma_j)}{[v^2(t-t_k)^2+\rho^2]^{n/2}} = E_{\alpha\beta}(t) .$$

Then

$$(3\text{-}12.20)\quad [\dot{H}_1(t)]_{\alpha\beta} = -\frac{n\hbar\, v^2(t-t_k)\, B_{\alpha\beta}(\sigma_j)}{[v^2(t-t_k)^2+\rho^2]^{n+2/2}} .$$

With (3-12.19) and (3-12.20), $C_{\beta\alpha}(t)$ becomes

$$C_{\beta\alpha}(t) = \frac{B_{\alpha\beta}(\sigma_j)}{A_{\alpha\beta}(\sigma_j)} \frac{nv^2}{\rho^2} \int_0^t dt'' \left\{ \frac{(t'' - t_k)}{\left[\frac{v^2(t'' - t_k)^2}{\rho^2} + 1\right]} \cdot \right.$$

(3-12.21)

$$\left. \cdot e^{-\frac{iA_{\alpha\beta}(\sigma_j)}{\rho^n} \int_0^{t''} \frac{dt'}{\left[\frac{v^2(t' - t_k)^2}{\rho^2} + 1\right]^{n/2}}} \right\} .$$

In the statistical approximation one is concerned with times that are small compared to the duration of a collision ($\Delta\tau \ll \tau_d$) so that one may neglect terms of the type

$$\frac{v^2(t - t_k)^2}{\rho^2}$$

in comparison to unity. Then, on shifting the time origin so that $t_k = 0$, one obtains the following expression for $C_{\beta\alpha}(\Delta\tau)$:

$$(3\text{-}12.22) \quad C_{\beta\alpha}(\Delta\tau) = \frac{B_{\beta\alpha}(\sigma_j)}{A_{\alpha\beta}(\sigma_j)} \frac{nv^2}{\rho^2} \int_{-\frac{\Delta\tau}{2}}^{\frac{\Delta\tau}{2}} dt \cdot t \cdot e^{-\frac{A_{\alpha\beta}(\sigma_j)t}{\rho^n}} .$$

Integrating yields

$$\left|C_{\beta\alpha}(\Delta\tau)\right| = \left| \frac{B_{\alpha\beta}(\sigma_j)n}{A_{\alpha\beta}(\sigma_j)} \left[\rho^{n-2} v^2 \frac{\Delta\tau}{A_{\alpha\beta}(\sigma_j)} \cos \frac{A_{\alpha\beta}(\sigma_j)\ \Delta\tau}{2\ \rho^n} \right.\right.$$

(3-12.23)

$$\left.\left. - \frac{2v^2\rho^{2(n-1)}}{A^2_{\alpha\beta}(\sigma_j)} \sin \frac{A_{\alpha\beta}(\sigma_j)\ \Delta\tau}{2\ \rho^n} \right] \right| .$$

Consider the first term in the bracket

$$(3\text{-}12.24) \quad \left| \frac{\rho^{n-2} v^2 \Delta\tau}{A_{\alpha\beta}(\sigma_j)} \cos \frac{A_{\alpha\beta}(\sigma_j)\ \Delta\tau}{2\ \rho^n} \right| < \left| \frac{\rho^{n-2} v^2 \Delta\tau}{A_{\alpha\beta}(\sigma_j)} \right| .$$

Also, since $\Delta\tau \ll \tau_d = 2\ \rho/v$, we have

$$(3\text{-}12.25) \qquad \left|\frac{\rho^{n-2}v^2\Delta\tau}{A_{\alpha\beta}(\sigma_j)} \cos \frac{A_{\alpha\beta}(\sigma_j)\Delta\tau}{2\rho^n}\right| \ll \left|\frac{2\rho^{n-1}v}{A_{\alpha\beta}(\sigma_j)}\right| .$$

In addition, the second term satisfies the inequality

$$(3\text{-}12.26) \qquad \left|2\left[\frac{v\rho^{n-1}}{A_{\alpha\beta}(\sigma_j)}\right]^2 \sin \frac{A_{\alpha\beta}(\sigma_j)\Delta\tau}{2\rho^n}\right| < 2\left|\left[\frac{v\rho^{n-1}}{A_{\alpha\beta}(\sigma_j)}\right]^2\right| .$$

In statistical limit it has been shown that $[v\rho^{n-1}/A_{\alpha\beta}(\sigma_j)] \ll 1$ so that $C_{\beta\alpha}(\Delta\tau)$ satisfies the following inequality:

$$(3\text{-}12.27) \qquad |C_{\beta\alpha}(\Delta\tau)| \ll \left|\frac{B_{\alpha\beta}(\sigma_j)n}{A_{\alpha\beta}(\sigma_j)}\right| .$$

It will be shown in Chapter V that $B_{\alpha\beta}(\sigma_j)$and $A_{\alpha\beta}(\sigma_j)$ are comparable numbers for hydrogen when the perturbers move very fast (e.g., electron collisions). For static perturbations the nondiagonal matrix elements of the perturbation vanish identically according to the usual theory of the first-order Stark effect.

Therefore, the ratio of $B_{\alpha\beta}(\sigma_j)$ and $A_{\alpha\beta}(\sigma_j)$ ranges from zero to about unity for perturber velocities ranging from zero to infinity. This means that the elements $|C_{\beta\alpha}(t)|$ are small compared to unity and approach zero in the static limit.

13. Phase-Shift Approximation

In the phase-shift approximation to the adiabatic theory of line broadening the phase integral $P_{na\alpha jk}(\tau)$ is replaced by the total phase change $P_{na\alpha jk}(\infty)$:

$$(3\text{-}13.1) \quad P_{na\alpha jk}(\tau) \to P_{na\alpha jk}(\infty) = \int_{-\infty}^{\infty} \frac{A_{a\alpha}(\sigma_j)\, dt}{[(t-t_k)^2 v_k^2 + \rho_j^2]^{n/2}} = \frac{A_{a\alpha}(\sigma_j)}{v_k \rho_j^{n-1}} \sqrt{\pi} \frac{\Gamma\left(\frac{n-1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)} .$$

This approximation is valid for the core of a spectral line for sufficiently weak interactions [small $A_{a\alpha}(\sigma_j)$ and/or high temperatures]. A validity criterion for the phase-shift limit will be derived in this section. These results will be applied in Chapter V to the problem of hydrogen line broadening by high-velocity electrons.

It is of interest to compare the mathematical basis of the (1) statistical and (2) phase-shift approximations to the adiabatic theory: (1) in the statistical limit one is concerned with frequencies (measured from the line center) that are high enough so that the Fourier integral expression for the line profile receives contributions from times $\Delta\tau$ that are much less than the time duration of the collision τ_d, i.e., the perturbing particles do not change their positions appreciably during the time $\Delta\tau$; (2) the phase-shift limit is valid for frequencies that are low enough so that the Fourier integral receives contributions from times $\Delta\tau$ that are much greater than the time duration of the collisions τ_d.

The phase integral $P_{na\alpha jk}(\tau)$ (3-12.1) can be written

$$(3\text{-}13.2) \qquad P_{na\alpha jk}(\tau) = \frac{A_{a\alpha}(\sigma_j)}{v_k^n} \int_{-t_k}^{\tau-t_k} \frac{dx}{x^n \left[1 + \left(\frac{\rho_j}{x v_k}\right)^2\right]^{n/2}} \, .$$

For $x > 0$ ($\tau < t_k$, $t_k > 0$), the integrand may be expanded in inverse powers of x:

$$P_{na\alpha jk}(\tau) = \frac{A_{a\alpha}(\sigma_j)}{v_k^n} \int_{-t_k}^{\tau-t_k} \frac{dx}{x^n} \left[1 - \frac{n}{2}\left(\frac{\rho_j}{x v_k}\right)^2\right] + \cdots$$

$$(3\text{-}13.3) \qquad = \frac{A_{a\alpha}(\sigma_j)}{v_k^n} \left[\frac{1}{(n-1)(\tau-t_k)^{n-1}} - \frac{1}{(n-1)(-t_k)^{n-1}} - + - \cdots\right]$$

$$\text{with} \qquad \tau < t_k, \; t_k > 0 \; .$$

For $x > 0$, ($\tau > t_k$, $t_k > 0$) the phase integral is written

$$P_{na\alpha jk}(\tau) = P_{na\alpha jk}(\infty) - \frac{A_{a\alpha}(\sigma_j)}{v_k^n}\left\{\int_{-\infty}^{-t_k} \frac{dx}{x^n\left[1 + \left(\frac{\rho_j}{v_k x}\right)^2\right]^{n/2}}\right.$$

(3-13.4)

$$\left. + \int_{\tau - t_k}^{\infty} \frac{dx}{x^n\left[1 + \left(\frac{\rho_j}{v_k x}\right)^2\right]^{n/2}}\right\} .$$

Again expanding the integrands by the binomial theorem and integrating term by term yields

$$P_{na\alpha jk}(\tau) = P_{na\alpha jk}(\infty) - \frac{A_{a\alpha}(\sigma_j)}{v_k^n}\left[\frac{1}{(n-1)(\tau - t_k)^{n-1}} - \frac{1}{(n-1)(-t_k)^{n-1}} - + \cdots\right]$$

(3-13.5)

with : $> t_k > 0$.

The main contribution to the integral arises from times in the neighborhood of $\tau = t_k$ so that with $\tau - t_k = \Delta\tau$, (3-13.5) and (3-13.3) become

(3-13.6) $$P_{na\alpha jk}(\tau > t_k) \cong P_{na\alpha jk}(\infty) - P_{na\alpha jk}(\tau < t_k) + \cdots$$

(3-13.7) $$P_{na\alpha jk}(\tau < t_k) \cong \frac{A_{a\alpha}(\sigma_j)}{v_k^n\,(n-1)(\Delta\tau)^{n-1}} + \cdots .$$

In the phase-shift approximation [$P_{na\alpha jk}(\tau) \cong P_{na\alpha jk}(\infty)$] it is required that

(3-13.8) $$\begin{aligned} |P_{na\alpha jk}(\tau < t_k)| &\ll 1 \\ |P_{na\alpha jk}(\tau < t_k)| &\ll |P_{na\alpha jk}(\infty)| . \end{aligned}$$

With (3-13.1), these two conditions lead to the following inequalities:

(3-13.9) $$\frac{1}{\Delta\tau} \sim \Delta\omega \ll \left[\frac{(n-1)v_k^n}{A_{a\alpha}(\sigma_j)}\right]^{\frac{1}{n-1}}$$

and

(3-13.10a) $$\frac{\Delta\tau}{\tau_d} \gg \frac{1}{2}\left[\frac{\Gamma\left(\frac{n}{2}\right)}{\sqrt{\pi}(n-1)\Gamma\left(\frac{n-1}{2}\right)}\right]^{\frac{1}{n-1}}$$

or

$$(3\text{-}13.10b) \qquad \frac{1}{\Delta\tau} \sim \Delta\omega \ll \left[\frac{\sqrt{\pi}(n-1)\Gamma\left(\frac{n-1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}\right]^{\frac{1}{n-1}} \frac{v_k}{\rho_j} \quad .$$

These inequalities restrict the phase-shift approximation to weak interactions [large impact parameters and small $A_{a\alpha}(\sigma_j)$] and high velocities or temperatures. In contrast to the statistical approximation, the condition (3-13.10a) demonstrates that the duration of a collision must be small compared to times of the order $(\Delta\omega)^{-1}$. The validity criterion (3-13.9) is essentially the same as that derived by Spitzer[9] by a different method.

The average phase factor (3-11.12) reduces to the following expression in the phase-shift approximation

$$(3\text{-}13.11) \qquad \left[e^{i\int_0^\tau (\Delta\omega_a - \Delta\omega_\alpha)dt}\right]_{Avg} = e^{-(\gamma_{a\alpha} - i\gamma'_{a\alpha})\tau} \quad .$$

The expressions $\gamma_{a\alpha}$ and $\gamma'_{a\alpha}$ are defined by

$$(3\text{-}13.12) \qquad \begin{pmatrix} -\gamma_{a\alpha} \\ \gamma'_{a\alpha} \end{pmatrix} \equiv \begin{pmatrix} R_e \\ I_m \end{pmatrix} 2\pi N \int_0^\infty W(v_k) v_k dv_k \int_0^\infty \rho_j d\rho_j \int_0^\Sigma \frac{d\sigma_j}{\Sigma} \left[e^{iP_{na\alpha jk}(\infty)} - 1\right] ,$$

where, subject to the validity criteria (3-13.8),

$$P_{na\alpha jk}(\tau) \rightarrow P_{na\alpha jk}(\infty) \text{ for } t_k < \tau; \int_0^\infty dt_k \rightarrow \tau \quad .$$

The equation (3-13.12) for $\gamma_{a\alpha}$ and $\gamma'_{a\alpha}$ contains a further approximation in that the integral over the velocity and impact parameter is extended from zero to infinity. This is inconsistent with the Spitzer inequality (3-13.9) since the phase-shift limit does not apply to collisions in which the velocity is near zero. However, it will be shown in Chapter V that the error introduced by this approximation is not significant for electron

broadening at high temperatures since the main contribution to the integral arises from velocities in the neighborhood of the average thermal velocity and from large impact parameters.

Our expression for the parameters $\gamma_{a\alpha}$ and $\gamma'_{a\alpha}$ reduces to the Lindholm[44]-Foley[32] half-width and shift parameters if $W(v)$ is taken to a delta function $\delta(v-\bar{v})$ where $\bar{v}$ is the average velocity. The errors introduced by this approximation are not entirely negligible (about 27 percent in the case of the first-order Stark broadening of hydrogen by electrons) and will also be discussed in detail later. It is also of some interest to point out that we have not restricted our derivation of the phase-shift theory to the consideration of a succession of single encounters. In deriving the expression (3-13.12) for $\gamma_{a\alpha}$ and $\gamma'_{a\alpha}$, the simultaneous interaction of many perturbers with the radiating atom was taken into account and is therefore somewhat more general than the derivations of other authors[10,11,14,32] who required the assumption of binary collisions and low densities in evaluating the phase-shift integrals.

The line profile corresponding to the phase-shift approximation is found by substituting the phase factor (3-11.12) into the Fourier integral (3-10.7), giving the well-known result

$$I_{a\alpha}(\omega) \frac{|\mu^o_{a\alpha}|^2}{\pi} R_e \int_0^\infty d\tau\, e^{-i\Delta\omega^o_{a\alpha}\tau - (\gamma_{a\alpha} - i\gamma'_{a\alpha})\tau}$$

$$= \frac{|\mu^o_{a\alpha}|^2}{\pi} \frac{\gamma_{a\alpha}}{(\Delta\omega^o_{a\alpha} - \gamma'_{a\alpha})^2 + (\gamma_{a\alpha})^2} \quad . \tag{3-13.13}$$

14. Nonadiabatic Effects in Degenerate Systems

Let us now consider the situation in which a group of spectral lines are not resolved with respect to their breadth. These lines are thought

to originate from transitions between the degenerate substates α and a of the initial and final states i and f. This presentation constitutes an extension to optical problems of the nonadiabatic impact theory worked out first by Anderson[14] and later by van Kranendonk,[48] using somewhat different methods. These authors were mainly concerned with the pressure broadening of microwave and infrared lines arising from dipole transitions between states i and f having angular momenta J_i and J_f. The theory was developed with the following basic assumptions: (1) the so-called impact assumption that the durations of the collisions are short compared to the time between them and (2) that only binary collisions are important. Both of these assumptions are highly restrictive for the problem at hand; namely, the broadening of spectral lines by ion and electron electric fields in a high-temperature plasma. The basic difficulties can be illustrated in the case of hydrogen line broadening by high-velocity electrons. The average duration of each collision $\bar{\tau}_d$ is of the order $2\bar{\rho}/\bar{v}$ (3-3.5), while the average time between collisions $\bar{\tau}_c$ is of the order

$$\bar{\tau}_c = \frac{1}{\pi \bar{\rho}^2 N_e \bar{v}} \quad . \tag{3-14.1}$$

The ratio $\bar{\tau}_d/\bar{\tau}_c$ is therefore of the order

$$\frac{\bar{\tau}_d}{\bar{\tau}_c} \simeq \frac{2\bar{\rho}^3 N_e}{\pi} \quad . \tag{3-14.2}$$

A typical interaction distance $\bar{\rho}$ can be taken to be of the order of the mean distance between electrons $\bar{\rho} \sim N_e^{-1/3}$ so that there is a significant number of collisions for which $\bar{\tau}_d/\bar{\tau}_c \simeq 1$. This argument is, of course, valid only for long-range interactions where distant collisions are important. Since the average time between collisions and typical collision times are of the same order of magnitude, the binary collision assumption

must also be viewed with caution.

The theoretical development of this section will be based on the expression (3-9.22) for the dipole matrix $\mu^c_{a\alpha}(t)$. It will be remembered that this matrix element was derived under the assumption that the expansion coefficients $C_{ba}(t)$ and $C_{\beta\alpha}(t)$ are small compared to unity. The case of "strong" collisions, where this approximation is no longer valid, must be considered separately and leads to the Lorentz type[49] of theory. However, it will turn out that the distant weak collisions are mainly responsible for the electron broadening.

If the initial and final states i and f are degenerate, then

$$\begin{aligned} \hbar\omega^o_{ab} &\equiv E^o_a - E^o_b = 0 \\ \hbar\omega^o_{\alpha\beta} &\equiv E^o_\alpha - E^o_\beta = 0 \quad . \end{aligned} \tag{3-14.3}$$

This condition allows great simplification of the formal theory. Substitution of our expression (3-9.22) for $\mu^c_{a\alpha}(t)$ into the Fourier integral (3-9.2) and using (3-14.3) yields the following intensity distribution:

$$I_{if}(\omega) \sum_{\alpha a} \frac{\rho_\alpha(0)}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_0^T dt\, e^{-i\Delta\omega^o_{if}t}\, \mu^o_{a\alpha} \left\{ e^{-P_{\alpha a}(t)} + \frac{\mu^o_{\alpha a}}{\mu^o_{a\alpha}} \left[\sum_\beta{}' \frac{\mu^o_{a\beta}}{\mu^o_{\alpha a}} C_{\beta\alpha}(t)\, e^{-iP_{\beta a}(t)} + \sum_b{}' \frac{\mu^o_{b\alpha}}{\mu^o_{\alpha a}} C^*_{ba}(t)\, e^{-iP_{\alpha b}(t)} \right] \right\} \right|^2_{\text{Avg}} , \tag{3-14.4}$$

where again

$\omega^o_{a\alpha} = \omega^o_{if} = \omega^o_i - \omega^o_f$ the unperturbed optical frequency

$\Delta\omega^o_{if} = \omega - \omega^o_{if}$ frequencies measured from ω^o_{if}

$P_{a\alpha}(t) \equiv P_{aa}(t) - P_{\alpha\alpha}(t) \equiv \int_0^t (\Delta\omega_a - \Delta\omega_\alpha)dt'$

$\mu^o_{\beta\alpha} \equiv$ unperturbed dipole matrix

$E_a(t) - E_\alpha(t) = \hbar\,(\omega^o_{if} + \Delta\omega_a - \Delta\omega_\alpha)$

$$C_{\beta\alpha}(t) = -\frac{1}{\hbar}\int_0^t \frac{[\dot{H}_1(t'')]_{\beta\alpha}}{\Delta\omega_\alpha - \Delta\omega_\beta}\left[\exp - i\int_0^{t''}(\Delta\omega_\alpha - \Delta\omega_\beta)dt\right] dt'' \quad .$$

Assuming that the collisions are weak so that $|C_{\beta\alpha}(t)| \ll 1$ and $|P_{a\alpha}(t)| \ll 1$, and keeping terms in (3-14.4) up to first order in these quantities, yields

$$I_{if}(\omega) = \sum_{a\alpha}\frac{\rho_\alpha(0)}{2\pi}|\mu^o_{a\alpha}|^2 \lim_{T\to\infty}\frac{1}{T}\left|\int_0^T dt\, e^{-i\Delta\omega^o_{if}t}\left\{1 - iP_{\alpha a}(t)\right.\right.$$

(3-14.5)

$$\left.\left. - \frac{i\,R_e}{|\mu^o_{a\alpha}|^2}\left[\sum_\beta{}' \mu^o_{a\beta}\, i\, C_{\beta\alpha}(t)\mu^o_{\alpha a} + \sum_b{}' \mu^o_{b\alpha}\, i\, C^*_{ba}(t)\,\mu^o_{\alpha a}\right]\right\}\right|^2_{Avg} \quad .$$

Consistent with the "weak collision" approximation this may also be written

$$(3\text{-}14.6) \qquad I_{if}(\omega) = \sum_{\alpha a}\frac{\rho_\alpha(0)|\mu^o_{a\alpha}|^2}{2\pi}\lim_{T\to\infty}\frac{1}{T}\left|\int_0^T dt\, e^{-i\Delta\omega^o_{if}t - i\Phi_{a\alpha}(t)}\right|^2_{Avg} \quad ,$$

where

$$\Phi_{a\alpha}(t) \equiv P_{\alpha a}(t) + \frac{R_e}{|\mu^o_{a\alpha}|^2}\left[\sum_\beta{}' \mu^o_{a\beta}\, i\, C_{\beta\alpha}(t)\mu^o_{\alpha a} + \sum_b{}' \mu^{o*}_{\alpha b}\, iC^*_{ba}(t)\mu^{o*}_{a\alpha}\right] \quad .$$

This formula is a generalization of the adiabatic theory in which the nondiagonal matrix elements of $H_1(t)$ were completely neglected. By the same arguments used to derive the adiabatic formula (3-10.7), one can write (3-14.6) in the usual correlation function form,

$$(3\text{-}14.7) \qquad I_{if}(\omega) = \sum_{a\alpha}\rho_\alpha(0)\frac{|\mu^o_{a\alpha}|^2}{\pi}R_e\int_0^\infty d\tau\, e^{-i\Delta\omega^o_{if}\tau}\left\{e^{-i\Phi_{a\alpha}(\tau)}\right\}_{Avg} \quad .$$

According to Section 13, in the limit of high velocities where times ($\Delta\tau \gg \tau_d$) contribute to the Fourier integral, one may replace

$$\frac{1}{\hbar}\int_0^t H_1(t')\,dt' \text{ by } \frac{1}{\hbar}\int_{-\infty}^{\infty} H_1(t')\,dt' \quad .$$

In this approximation we have

$$P_{a\alpha}(\tau) \to \frac{1}{i\hbar}\int_{-\infty}^{\infty} [H_1(t)]_{aa}\, dt - \frac{1}{i\hbar}\int_{-\infty}^{\infty} [H_1(t)]_{\alpha\alpha}\, dt$$

$$(3\text{-}14.8)\quad C_{\beta\alpha}(\tau) \to -\frac{i}{\hbar}\int_{-\infty}^{\infty} [H_1(t)]_{\beta\alpha}\, e^{iP_{\beta\alpha}(t')}\, dt \equiv -i\phi_{\beta\alpha}$$

$$\phi_{\alpha\alpha} \equiv \frac{1}{i\hbar}\int_{-\infty}^{\infty} [H_1(t)]_{\alpha\alpha}\, e^{iP_{\alpha\alpha}(t)}\, dt = \frac{1}{i\hbar}\int_{-\infty}^{\infty} [H_1(t)]_{\alpha\alpha}\, dt\ ,$$

where we have simplified the notation by introducing the matrix $\phi_{\beta\alpha}$ defined above. In the high-velocity approximation $\Phi_{a\alpha}(\tau)$ is now

$$(3\text{-}14.9)\quad \Phi_{a\alpha}(\tau) \to \Phi_{a\alpha}(\infty) = \frac{R_e}{|\mu^o_{a\alpha}|^2}\sum_{\beta,b}(\mu^o_{a\beta}\phi_{\beta\alpha}\mu_{\alpha a}) - (\mu^o_{\alpha b}\phi_{ba}\mu^o_{a\alpha})^*\ .$$

The final expression for $I_{if}(\omega)$ can now be found from (3-14.7) with (3-14.9) by putting $\exp -i\Phi_{a\alpha}(\infty) \cong 1 - i\Phi_{a\alpha}(\infty)$ [since $|\Phi_{a\alpha}(\infty)| \ll 1$ in the weak collision theory]:

$$I_{if}(\omega) = \frac{\rho_\alpha(0)}{\pi}\sum_{\alpha a}|\mu^o_{a\alpha}|^2 R_e\int_0^\infty dt\, e^{-i\Delta\omega_{if}\tau}\,[1 - i\Phi_{a\alpha}(\infty)]_{Avg}$$

$$(3\text{-}14.10)\quad = \frac{\rho_\alpha(0)}{\pi}\, R_e\int_0^\infty d\tau\, e^{-i\Delta\omega_{if}\tau}\,[\sum_{\alpha a}|\mu^o_{a\alpha}|^2 - i\sum_{\alpha a}|\mu^o_{a\alpha}|^2\,\Phi_{a\alpha}(\infty)]_{Avg}$$

$$(3\text{-}14.11)\quad = \frac{\rho_\alpha(0)}{\pi}\Big(\sum_{\alpha a}|\mu^o_{a\alpha}|^2\Big)R_e\int_0^\infty dt\, e^{-i\Delta\omega^o_{if}\tau}\left[1 - \frac{i\sum_{\alpha a}|\mu^o_{a\alpha}|^2\,\Phi_{a\alpha}(\infty)}{\sum_{\alpha a}|\mu^o_{a\alpha}|^2}\right]_{Avg}$$

so that

$$(3\text{-}14.12)\qquad I_{if}(\omega) = \frac{\rho_\alpha(0)}{\pi}\sum_{\alpha a}|\mu^o_{a\alpha}|^2 R_e\int_o^\infty d\tau\, e^{-i\Delta\omega^o_{if}\tau}\left[e^{\frac{-i\sum_{\alpha a}|\mu^o_{a\alpha}|^2\Phi_{a\alpha}(\infty)}{\sum_{a\alpha}|\mu^o_{a\alpha}|^2}}\right]_{Avg}$$

with (3-14.6) it follows that

$$(3\text{-}14.13)\qquad \frac{\sum_{a\alpha}|\mu^o_{a\alpha}|^2\Phi_{a\alpha}(\infty)}{\sum_{a\alpha}|\mu^o_{a\alpha}|^2} = \frac{\sum_{a\alpha b\beta}(\mu^o_{a\beta}\phi_{\beta\alpha}\mu_{\alpha a}) - (\mu_{\alpha a}\phi_{ab}\mu_{b\alpha})}{\sum_{a\alpha}|\mu^o_{a\alpha}|^2}\,.$$

This is the Anderson impact formula.[14] It can be used to describe optical transitions between degenerate initial and final states as well as transitions between rotational states giving rise to microwave and infrared spectral lines. However, in addition, this derivation does not contain the usual assumption that the mean time between collisions is small compared to the time duration of the collision. This generalization is important for Coulomb interactions.

Now, to <u>first order</u> in $H_1(t)$, we have with (3-14.8) and (3-14.9)

$$\sum_{a\alpha}|\mu^o_{a\alpha}|^2\Phi_{a\alpha}(\infty) = \frac{1}{\hbar}\int_{-\infty}^{\infty}dt\Big\{\Big(\sum_{a\alpha b\beta}\mu^o_{a\beta}\,[H_1(t)]_{\beta\alpha}\,\mu_{\alpha a}\Big)$$

$$(3\text{-}14.14)\qquad -\Big(\mu^o_{\alpha a}\,[H_1(t)]_{ab}\,\mu^o_{b\alpha}\Big)\Big\}\,.$$

If $H_1(t)$ is a scalar sum over all the perturbers, then the statistical considerations of Sections 11 and 13 of this chapter apply directly to the general nonadiabatic case since the phase factors

$$\left[e^{\,i\sum_{a\alpha}|\mu^o_{a\alpha}|^2\Phi_{a\alpha}(\infty)/\sum_{a\alpha}|\mu^o_{a\alpha}|^2}\right]_{Avg}$$

can again be written as a product of individual collision phase factors. The method of evaluating (3-14.11) is then identical to the adiabatic case and the absorption coefficient is given by

$$(3\text{-}14.15) \qquad I_{if}(\omega) = \frac{\rho_\alpha(0)}{\pi}\left(\sum_{\alpha a} |\mu^o_{a\alpha}|^2\right)\left[\frac{\gamma_1}{(\omega-\omega^o_{if}-\gamma_2)^2+\gamma_1^2} + \frac{\gamma_1}{(\omega+\omega^o_{if}-\gamma_2)^2+\gamma_1^2}\right],$$

where γ_1 and γ_2 are the real and imaginary parts of

$$(3\text{-}14.16) \qquad \begin{Bmatrix}-\gamma_1\\ \gamma_2\end{Bmatrix} = \begin{Bmatrix}R_e\\ I_m\end{Bmatrix}\int_o^\infty 2\pi N v W(v)dv \int_o^\infty \rho d\rho \int_o^\Sigma \frac{d\sigma}{\Sigma}\left[\exp \frac{-i\sum_{a\alpha}\Phi_{na\alpha jk}(\infty)|\mu^o_{a\alpha}|^2}{\sum_{a\alpha}|\mu^o_{a\alpha}|^2} - 1\right].$$

The above expression* is valid for scalarly additive multiple interactions. For completeness we have included the nonresonant term in (3-14.15), which follows from the general intensity distribution (3-7.3). The result (3-14.15), which has been derived on the basis of the weak collision hypothesis [small phase shifts and amplitudes $C_{ba}(t)$ and $C_{\beta\alpha}(t)$], is of the same form as given by the "strong binary collision"[50] theory of line broadening in which $1/\gamma_1$ is replaced by τ_c, the mean time between collisions. There is a slight difference, however, in that the more distant weak interactions can cause a shift in the frequency maximum corresponding to γ_2. The Van Vleck-Weisskopf theory[50] does not contain a shift ($\gamma_2=0$). Because of the fact that the strong and weak collision theories yield such similar results near the line center, it is extremely difficult to determine intermolecular forces from line broadening data alone. Both strong and weak collisions can be taken into account approximately by considering two types of collisions with impact parameters ranging from $0\rightarrow\rho_c$ and $\rho_c\rightarrow\infty$. The impact parameter ρ_c separating the two regions is chosen such that the matrix element of the phase integral is unity. The weak collision theory fails for close collisions with such large matrix elements since each collision can be considered to induce a transition

*$\Phi_{a\alpha}(\infty) = \sum_{jk} \Phi_{na\alpha jk}(\infty)$, where $\Phi_{na\alpha jk}(\infty)$ is the contribution of a single collision to $\Phi_{a\alpha}(\infty)$.

with nearly unit probability. That is, for $\rho < \rho_c$ the contribution to the half-width according to the strong collision theory is just the mean time between collisions. For collisions with $\rho > \rho_c$ the weak collision theory developed here is assumed to be applicable.

$$(3\text{-}14.17) \qquad (\gamma_1)_{\rho < \rho_c} = \frac{1}{\tau_c} = \pi \rho_c^2 N \bar{v}$$

$$(3\text{-}14.18) \qquad (\gamma_1)_{\rho > \rho_c} = - R_e \int_0^\infty 2\pi N v W(v)\, dv \int_{\rho_c}^\infty \rho d\rho \int_0^{\Sigma} \frac{d\sigma}{\Sigma} \left[\exp \frac{-i \sum_{a\alpha} \Phi_{na\alpha jk}(\infty) |\mu^o_{a\alpha}|^2}{\sum_{a\alpha} |\mu^o_{a\alpha}|^2} - 1 \right]$$

$$(3\text{-}14.19) \qquad \gamma_1 = (\gamma_1)_{\rho < \rho_c} + (\gamma_1)_{\rho > \rho_c} ,$$

where ρ_c is to be determined from

$$(3\text{-}14.20) \qquad P_{a\alpha}(\infty) = 1 \text{ (unit phase shift)}.$$

Collisions with $\rho \sim \rho_c$ are clearly treated incorrectly because our interpolation procedure is of doubtful validity in that region. A more exact theory would require the solution of the set of coupled differential equations (3-9.5). This is prohibitively difficult if many eigenstates are involved, as there are in the degenerate levels of hydrogen. However, if either strong or weak collisions are mainly responsible for the broadening, the above method of approximation is probably fairly accurate. This interpolation scheme is somewhat simpler than that proposed by Anderson.[14]

In the above derivation of the line broadening to be expected in the optical region for transitions between degenerate states, it was assumed that $\omega^o_{\alpha\beta}$ is zero (the condition of degeneracy) in the expression (3-9.22) for the dipole matrix $\mu^c_{a\alpha}(t)$. If the degenerate

splitting is not zero, but small in comparison to the width of the line, then the theory is still applicable. To show this, consider the frequency $\Delta\omega^{o}_{a\beta}$ defined by

$$(3\text{-}14.21) \qquad \Delta\omega^{o}_{\alpha\beta} \equiv \omega-\omega^{o}_{a} + \omega^{o}_{\beta} \equiv \omega - \omega^{o}_{a\beta} = \omega - \omega^{o}_{a\alpha} + \omega^{o}_{\beta\alpha} = \Delta\omega^{o}_{a\alpha} + \omega^{o}_{\beta\alpha}$$

For frequencies much greater than the degenerate splitting $(\Delta\omega^{o}_{\alpha\beta} \gg \omega_{\beta\alpha})$ we have

$$(3\text{-}14.22) \qquad \Delta\omega^{o}_{a\beta} \sim \Delta\omega^{o}_{a\alpha} ,$$

so that $\Delta\omega^{o}_{a\beta}$ can be taken to be independent of the degenerate indices when the line width is much greater than the degenerate splitting. This approximation leads directly to the nonadiabatic formalism of this section.

These results can be used to estimate the nonadiabatic effects due to electron collisions in calculating the shape of the Balmer lines in the far wings ($\Delta\omega$ large compared to the average static splitting of the Balmer levels due to ion fields). The situation when the static field splitting and $\Delta\omega^{o}_{\alpha\beta}$ are comparable (the core of the Balmer lines) leads to a much more complicated theory and will be discussed in the next section. The formal results which will be obtained are similar to those of Spitzer,[9] who considered the broadening of Lyman α in an ionized gas.

15. Nonadiabatic Effects in Nearly Degenerate Systems

The results of the previous section will now be generalized to take into account transitions between nearly degenerate substates of an initial state* i and a final state f. By nearly degenerate is meant that $\hbar\,\omega^{o}_{ab}$ and $\hbar\,\omega^{o}_{\alpha\beta}$ are not necessarily zero but small compared to the kinetic energy of the perturbing particles. Considerations of this type are relevant to

*The substates of i are denoted by the subscript α and those of f by a, as in previous sections.

the problem of hydrogen line broadening by both ions and electrons. The slow-moving ions produce a static electric field which removes the normal hydrogen degeneracy. The static splitting ω^{o}_{ab}, $\omega^{o}_{\alpha\beta}$ can be calculated by the ordinary theory of the Stark effect and averages over this splitting can be performed with the usual Holtsmark probability function (see Chapter V).

According to the weak collision theory, the time-dependent dipole matrix is found from (3-9.22):

$$\mu_{a\alpha}(t) = \mu^{o}_{a\alpha}\, e^{i\omega^{o}_{a\alpha}t}\,[1 + iP_{a\alpha}(t)] + \sum_{\beta}{}' \mu^{o}_{a\beta}\, C_{\beta\alpha}(t)\, e^{i\omega^{o}_{a\beta}t} + \sum_{\beta}{}' \mu^{o}_{b\alpha}\, C^{*}_{ba}(t)\, e^{i\omega^{o}_{b\alpha}t} \tag{3-15.1}$$

Exponentials of the type $\exp iP_{a\alpha}(t)$ were approximated by $[1+iP_{a\alpha}(t)]$ in the expression (3-9.22) for $\mu_{a\alpha}(t)$ and terms of the order $P_{a\alpha}(t)\, C_{\beta\alpha}(t)$ were neglected in first order. This is consistent with the weak collision theory in which $|P_{a\alpha}(t)|$ and $|C_{\beta\alpha}(t)|$ are assumed to be small compared to unity. This approximation was also employed in the theory (previous section) for transitions between degenerate initial and final states.

The absorption coefficient is found by substituting the dipole matrix (3-15.1) into the Fourier integral expression (3-9.2) for the line shape:

$$I_{a\alpha}(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_{o}^{T} dt \left\{ \mu^{o}_{a\alpha}\, e^{-i\Delta\omega^{o}_{a\alpha}(t)}\,[1 + i\, P_{a\alpha}(t)] + \sum_{\beta}{}' \mu^{o}_{b\alpha}\, C^{*}_{ba}(t)\, e^{-i\Delta\omega^{o}_{b\alpha}t} + \sum_{\beta}{}' \mu^{o}_{a\beta}\, C_{\beta\alpha}(t)\, e^{-i\Delta\omega^{o}_{a\beta}t} \right\} \right|^{2}_{\text{Avg}} . \tag{3-15.2}$$

To proceed further, consider a typical term in this equation:

$$(3\text{-}15.3)\quad \tilde{C}_{\beta\alpha} \equiv \mu^{o}_{a\beta}\int_{o}^{T} dt\; C_{\beta\alpha}(t)\, e^{-i\Delta\omega^{o}_{\alpha\beta}t}, \quad \tilde{C}^{*}_{ba} \equiv \mu^{o}_{b\alpha}\int_{o}^{T} dt\; C^{*}_{ba}(t)\, e^{-i\Delta\omega^{o}_{b\alpha}t}.$$

The expansion coefficient $C_{\beta\alpha}(t)$ is given to first order in $H_1(t)$ by (see 3-9.12)

$$(3\text{-}15.4)\quad C_{\beta\alpha}(t) = -\frac{i}{\hbar}\int_{o}^{t} dt'\; [H_1(t')]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}t'} \qquad t \gg \tau_d .$$

This expression for $C_{\beta\alpha}(t)$ is valid for times which are large compared to the duration of a collision.

For scalarly additive perturbations, $H_1(t)$ is a sum over all collisions with times of closest approach t_k, velocities v_k, impact parameters ρ_j, etc.

$$(3\text{-}15.5)\qquad H_1(t) = \sum_{k,j} H_j(t-t_k) .$$

The typical term (3-15.3) can now be written with (3-15.4) and (3-15.5):

$$(3\text{-}15.6)\quad \tilde{C}_{\beta\alpha} = \frac{-i}{\hbar}\,\mu^{o}_{a\beta}\sum_{kj}\int_{o}^{T} dt\; e^{-i\Delta\omega^{o}_{a\beta}t}\int_{o}^{t} dt'\; [H_j(t'-t_k)]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}t'} .$$

Letting $t'-t_k=\tau'$ and $t-t_k=\tau$ yields

$$(3\text{-}15.7)\quad \tilde{C}_{\beta\alpha} = \frac{-i}{\hbar}\,\mu^{o}_{a\beta}\sum_{kj} e^{-i\Delta\omega^{o}_{a\alpha}t_k}\int_{-t_k}^{T-t_k} d\tau\; e^{-i\Delta\omega^{o}_{\alpha\beta}\tau} \cdot \int_{-t_k}^{\tau} d\tau'\; [H_j(\tau')]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}\tau'} .$$

A partial integration gives

$$\tilde{C}_{\beta\alpha} = -\frac{\mu^{o}_{\alpha\beta}}{\hbar\Delta\omega^{o}_{\alpha\beta}} \sum_{kj} \left\{ e^{-i\Delta\omega^{o}_{a\alpha}t_k} \int_{-t_k}^{T-t_k} d\tau [H_j(\tau)]_{\beta\alpha}\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \right.$$

(3-15.8)

$$\left. -e^{-i\Delta\omega^{o}_{a\alpha}T} \int_{-t_k}^{T-t_k} d\tau [H_j(\tau)]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}\tau} \right\} .$$

In the phase-shift approximation, where one neglects the duration of each collision, $\tilde{C}_{\beta\alpha}$ becomes

$$\tilde{C}_{\beta\alpha} = -\frac{\mu^{o}_{a\beta}}{\hbar\Delta\omega^{o}_{a\beta}} \sum_{j,v_k} \int_{o}^{T} e^{-i\Delta\omega^{o}_{a\alpha}t} dt \int_{-\infty}^{\infty} d\tau [H_j(\tau)]_{\beta\alpha}\, e^{-i\Delta\omega^{o}_{a\alpha}\tau}$$

(3-15.9)

$$-e^{-i\Delta\omega^{o}_{a\alpha}T} \sum_{kj} \int_{-\infty}^{\infty} d\tau\, [H_j(\tau)]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}\tau} ,$$

where the sum over t_k has been replaced by an integral.

Substituting terms of this form into the Fourier integral (3-15.2), and taking the square of the absolute value, yields a delta function from the first term in (3-15.9):

$$\frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_{o}^{T} dt\, e^{-i\Delta\omega^{o}_{a\alpha}t} \right|^2 = \delta(\Delta\omega^{o}_{a\alpha}) . \qquad (3\text{-}15.10)$$

This function is zero for frequencies $\Delta\omega^{o}_{a\alpha} \neq 0$. In addition, cross terms involving $\exp -i\Delta\omega^{o}_{a\alpha}T$ do not contribute to any time averages over finite time intervals. For these reasons $\tilde{C}_{\beta\alpha}$ can be written*

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*Similarly, $\tilde{C}^{*}_{ba}$ is given by

$$\tilde{C}^{*}_{ba} = -\frac{\mu^{o}_{b\alpha}}{\hbar\Delta\omega^{o}_{b\alpha}} \sum_{kj} \int_{-\infty}^{\infty} d\tau\, [H_j(\tau)]_{ab}\, e^{+i\omega^{o}_{ab}\tau} .$$

$$(3\text{-}15.11)\qquad \tilde{C}_{\beta\alpha} = \frac{\mu^{o}_{a\beta}}{\hbar\Delta\omega^{o}_{a\beta}} \sum_{kj} \int_{-\infty}^{\infty} d\tau [H_j(\tau)]_{\beta\alpha}\, e^{-i\omega^{o}_{\alpha\beta}\tau} \quad \text{for } \Delta\omega^{o}_{a\alpha} \neq 0 .$$

One can now give a physical interpretation of this result. The atomic system is initially in the state α. A time-dependent perturbation causes a transition $\alpha \to \beta$ with the subsequent emission of a photon resulting from a transition to a final state $\underline{a}$. The term $\tilde{C}_{\beta\alpha}$ takes into account these processes. The divergence at $\Delta\omega^{o}_{\alpha\beta}=0$ reflects a lack of refinement in our analysis, which can be traced to our weak collision approximation. This approximation requires that matrix elements of the phase integral, summed over all collisions, be small compared to unity. For large times this approximation fails due to the cumulative effect of many collisions. The large-time behavior of these matrix elements determines the behavior of the absorption coefficient near resonance. This follows from general considerations of the properties of Fourier integrals.

The absorption coefficient (3-15.2) can now be expressed in terms of the $\tilde{C}_{\beta\alpha}$:

$$I_{a\alpha}(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \sum_{t_k} \sum_{j v_k} \frac{1}{T} \left| \sum_{\beta}{}' \tilde{C}_{\beta\alpha} + \sum_{b}{}' \tilde{C}^{*}_{ba} \right|^{2}_{\text{Avg}}$$

$$(3\text{-}15.12)$$

$$= \frac{1}{2\pi} \sum_{j, v_k} \left| \sum_{\beta}{}' \tilde{C}_{\beta\alpha} + \sum_{b}{}' \tilde{C}^{*}_{ba} \right|^{2}_{\text{Avg}} .$$

In the adiabatic case, the nondiagonal elements are taken to be zero and the above expression reduces to

$$[I_{a\alpha}(\omega)]_{Ad} = \frac{1}{2\pi}\sum_{j,v_k}\left|\tilde{C}_{\alpha\alpha} + \tilde{C}_{aa}\right|^2$$

(3-15.13)
$$= \frac{|\mu^o_{a\alpha}|^2}{\pi(\Delta\omega^o_{a\alpha})^2}\sum_{jv_k}\frac{1}{2\hbar^2}\left\{\int_{-\infty}^{\infty}\left([H_j(\tau)]_{\alpha\alpha} - [H_j(\tau)]_{aa}\right)d\tau\right\}^2_{Avg} .$$

This result is to be compared with the results of Section III.13 where, according to (3-13.13),

(3-15.14) $$[I_{a\alpha}(\omega)]_{Ad} = \frac{|\mu^o_{a\alpha}|^2}{\pi}\frac{\gamma_{a\alpha}}{(\Delta\omega^o_{a\alpha})^2}, |\Delta\omega^o_{a\alpha}| \gg \gamma_{a\alpha}, \gamma'_{a\alpha} .$$

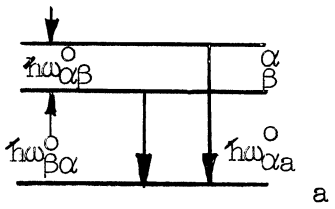
The half-width parameter $\gamma_{a\alpha}$ can be written (see 3-13.12 and 3-13.1):

$$\gamma_{a\alpha} = -2\pi N R_e\int_0^{\infty}W(v_k)v_k dv_k\int_0^{\infty}\rho_j d\rho_j\int_0^{\Sigma d\sigma_j/\Sigma}\left[e^{iP_{na\alpha jk}(\infty)} - 1\right]$$

(3-15.15)
$$= R_e\sum_{v_k,j}\left\{1 - e^{-\frac{i}{\hbar}\int_{-\infty}^{\infty}\left([H_j(\tau)]_{aa} - [H_j(\tau)]_{\alpha\alpha}\right)d\tau}\right\}_{Avg}$$

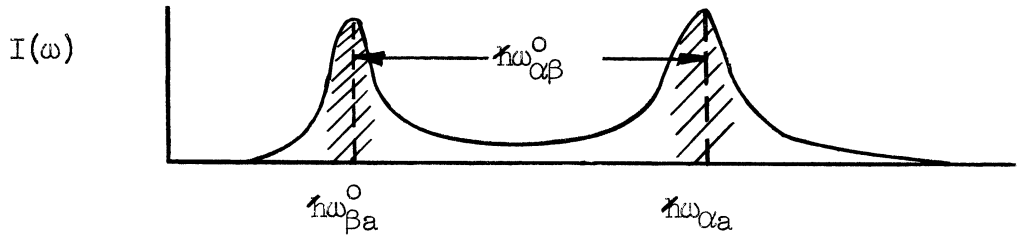
$$= \frac{1}{2\hbar^2}\sum_{j,v_k}\left\{\int_{-\infty}^{\infty}\left([H_j(\tau)]_{aa} - [H_j(\tau)]_{\alpha\alpha}\right)d\tau\right\}^2_{Avg} + \cdots .$$

The two results (3-15.15), (3-15.14) and (3-15.13) agree with one another to first order in the phase integrals. Since our expansion procedure for the weak collision approximation requires this approximation, the two results are consistent. It is therefore evident that the formula (3-15.12) is valid for frequencies which are large compared to the half-width. For example, consider a three-state atom with an energy-level diagram of the type



a

and spectral lines with the general appearance



The nonadiabatic theory developed here is not valid for the shaded portion of the lines, i.e., near resonance. Furthermore, the splitting $\hbar\omega^o_{\alpha\beta}$ must be small compared to the kinetic energy of the perturbers in the classical path approximation.

The results of this section constitute a generalization of a theory due to Spitzer[9] for transitions between a doubly degenerate state and a nondegenerate S-state if we put

$$[H_j(\tau)]_{ab} = 0 \quad \text{(nondegenerate final state)}$$

$$|\mu^o_{a\alpha}|^2 = |\mu^o_{a\beta}|^2 \quad \text{(lines of equal intensity)} \tag{3-15.16}$$

$$\omega^o_{\alpha\beta} = 0 \quad \text{(no degenerate fine structure)}$$

and furthermore neglect all cross products in (3-15.12). The assumption that the final state be nondegenerate restricts the applicability of the Spitzer impact formula to the Lyman series in the case of hydrogen. The assumption that all the dipole matrix elements $|\mu^o_{a\alpha}|$ are equal restricts the theory to a composite of lines for which the line strengths are all equal. This condition is not satisfied for hydrogen since the various Stark components have, in general, different strengths. Finally, the

condition that there be no degenerate splitting restricts the theory to the case in which there is no static perturbation field due to ions. To include both ions and electrons in the theory of hydrogen line broadening, the static ion field is important and cannot be neglected. These results will be applied to Lyman α line in Chapter V and a procedure for calculating Balmer line profiles will be outlined.

This completes our discussion of the formal aspects of the classical path theory of line broadening for weak interactions. We will now proceed to a discussion of some explicit calculations by various authors in connection with the theory of hydrogen line broadening by ions and electrons. This historical résumé was postponed so that we could compare the different theories with the formulation given in the present chapter.

CHAPTER IV

PREVIOUS THEORIES OF HYDROGEN LINE BROADENING

1. The Holtsmark Statistical Theory

In this chapter various classical path theories of line broadening will be reviewed. It is not our purpose to give a comprehensive summary of the entire subject but to focus our main attention on those aspects of the problem which pertain to hydrogen line broadening in a partially ionized gas at high temperature. The relationship between the theories and experimental observations will also be discussed.

Holtsmark[5] recognized the need for a theory of spectral line broadening which took into account explicitly the interaction between a radiating atom and the perturbing particles. He was dissatisfied with the earlier classical theory of Lorentz,[49] who conceived of collision broadening as arising from the interruption of a continuous wave train at each collision. Prompted by the then recent experiments of Stark[51] on the shift and splitting of spectral lines in an external static electric field, Holtsmark calculated the probability distribution of the strength of the field produced by a static random distribution of ions, dipoles, or quadrupoles. We are interested only in ion broadening here and will therefore omit a discussion of dipole and quadrupole interactions. The justification of the static approximation for ions follows from the Holstein inequality[47] given in Section III.12. Further discussion of this point will be given in the next chapter. The Holtsmark theory for broadening by static ion fields, however, is not valid for electron broadening

because of the large average velocity.

Holtsmark based his calculations on the Markoff[45] method* of calculating statistical distribution functions. Because of the importance of the Holtsmark theory in practical applications, the basic theory will be given here also, but from a slightly different point of view. The statistical theory follows as a special case of the classical path theory of line broadening developed in the previous chapter, so it is convenient to adopt the notation and ideas embodied in the Fourier integral formalism. The results to be obtained are, of course, identical to those of the Markoff type theory.

It was shown in Section III.10, that the statistical approximation follows from the adiabatic distribution function

$$(3\text{-}10.5) \qquad I_{a\alpha}(\omega) = |\mu^{o}_{a\alpha}|^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{i\int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt} \right]_{Avg} ,$$

when the phase integral is evaluated in the statistical limit by taking the velocity of the perturbers to be zero:

$$(4\text{-}1.1) \qquad \lim_{v \to 0} \int_{o}^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt = (\Delta\omega_a - \Delta\omega_\alpha)\tau \ .$$

The adiabatic formula for the absorption coefficient is now reduced to

$$(4\text{-}1.2) \qquad I_{a\alpha}(\omega) = |\mu^{o}_{a\alpha}|^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \left[e^{-i(\Delta\omega^{o}_{a\alpha} + \Delta\omega_\alpha - \Delta\omega_a)\tau} \right]_{Avg} .$$

The case of scalarly additive perturbations was discussed in Chapter III and the perturbation was written in the form

$$\Delta\omega_a - \Delta\omega_\alpha = \sum_{kj} (\Delta\omega_a - \Delta\omega_\alpha)_{kj} \ .$$

*See the excellent review article of Chandrasekhar, Ref. 46.

The averaging procedure was also given for this situation. Suppose now that a spectral line arising from a transition between the states (i,a) and (f,α) is shifted due to the presence of a static electric field and that the shift is proportional to the absolute magnitude of the instantaneous field strength $|\vec{F}| \equiv F$. For hydrogen the shift can be calculated from the relation given in Section III.5:

$$\Delta E = \frac{3}{2} n(k_1-k_2)\, e\, a_o\, F \tag{3-5.9}$$

The field strength F is given by the absolute value of the vector sum of the individual ion fields:

$$F = \left| e \sum_{jk} \frac{\vec{r}_j(t-t_k)}{[r_j(t-t_k)]^3} \right| ; \quad |r_j(t-t_k)|^2 = v_k^2(t-t_k)^2 + \rho_j^2 \quad . \tag{4-1.3}$$

For time-independent field strength F is given by

$$\lim_{v_k \to 0} F = \left| e \sum_j \frac{\rho_j}{\rho_j^3} \right| \tag{4-1.4}$$

and the phase integral becomes

$$\begin{aligned} \int_0^\tau (\Delta\omega_a - \Delta\omega_\alpha)dt &= \tau \frac{3}{2} \frac{e^2 a_o}{\hbar} \left\{ [n(k_1-k_2)]_a - [n(k_1-k_2)]_\alpha \right\} \left| \sum_j \frac{\vec{\rho}_j}{\rho_j^3} \right| \\ &\equiv AX_{a\alpha} \left| \sum_j \frac{\vec{\rho}_j}{\rho_j^3} \right| \tau \quad , \end{aligned} \tag{4-1.5}$$

where A and $X_{a\alpha}$ are defined by

$$A \equiv \frac{3}{2} \frac{e^2 a_o}{\hbar} ; \quad X_{a\alpha} \equiv [n(k_1-k_2)]_a - [n(k_1-k_2)]_\alpha \quad . \tag{4-1.6}$$

The absorption coefficient corresponding to this type of interaction is then

$$I_{a\alpha}(\omega)d\omega = \frac{|\mu^o_{a\alpha}|^2}{AX_{a\alpha}} \frac{d\omega}{2\pi} \int_{-\infty}^{\infty} d\tilde{z} \left[e^{-i\left(\frac{\Delta\omega^o_{a\alpha}}{AX_{a\alpha}} - \left| \sum_j \frac{\vec{\rho}_j}{\rho_j^3} \right| \right) z} \right]_{Avg} \tag{4-1.7}$$

$$z \equiv AX_{a\alpha}\, \tau \quad .$$

For convenience let us define a vector $\vec{\Lambda}$ in the direction of $\vec{F}$ whose magnitude is

$$(4\text{-}1.8) \qquad |\vec{\Lambda}| \equiv \frac{\Delta\omega^{o}_{a\alpha}}{AX_{a\alpha}} \equiv \frac{\omega-\omega^{o}_{a\alpha}}{AX_{a\alpha}} \ ;$$

then

$$(4\text{-}1.9) \qquad d\,|\vec{\Lambda}| = \frac{d\omega}{AX_{a\alpha}} \ .$$

The absorption coefficient may be expressed in terms of $|\vec{\Lambda}|$:

$$(4\text{-}1.10) \qquad \begin{aligned} I_{a\alpha}(|\vec{\Lambda}|)d|\vec{\Lambda}| &= |\mu^{o}_{a\alpha}|^2 \ \frac{d|\vec{\Lambda}|}{2\pi} \int_{-\infty}^{\infty} d\xi \left[e^{-i\left(\left|\vec{\Lambda} - \sum_j \frac{\vec{\rho}_j}{\rho_j^3}\right|\right)z} \right]_{Avg} \\ &\equiv |\mu^{o}_{a\alpha}|^2 \ d|\vec{\Lambda}| \ W(|\vec{\Lambda}|) \ . \end{aligned}$$

Consider now the probability distribution of the x component of $\vec{\Lambda}$:

$$(4\text{-}1.11) \qquad W(\Lambda_x)d\Lambda_x = \frac{d\Lambda_x}{2\pi} \int_{-\infty}^{\infty} d\xi \left\{ e^{-i\left[\Lambda_x - \sum_j \frac{(\vec{\rho}_j)_x}{\rho_j^3}\right]\xi} \right\}_{Avg} \ ,$$

and similarly for the y and z components. The distribution $W(\vec{\Lambda})\ d\vec{\Lambda}$ of $\vec{\Lambda}$ is given by the product

$$(4\text{-}1.12) \qquad W(\vec{\Lambda})d\vec{\Lambda} = W(\Lambda_x)W(\Lambda_y)W(\Lambda_z)d\Lambda_x d\Lambda_y d\Lambda_z \ .$$

Since the distribution $W(\vec{\Lambda})$ is independent of angles for an isotropic ion distribution, the scalar distribution $W(|\vec{\Lambda}|)$ is found by transforming to polar coordinates

$$(4\text{-}1.13) \qquad d\Lambda_x d\Lambda_y d\Lambda_z = d\Omega |\vec{\Lambda}|^2 \ d|\vec{\Lambda}|$$

and integrating over the solid angle $d\Omega$

$$(4\text{-}1.14) \qquad W(|\vec{\Lambda}|)\ d|\vec{\Lambda}| = \int_0^{4\pi} d\Omega |\vec{\Lambda}|^2 \ d|\vec{\Lambda}| \ W(\vec{\Lambda}) = 4\pi W(\vec{\Lambda}) |\vec{\Lambda}|^2 \ d|\vec{\Lambda}| \ .$$

The distribution function $W(|\vec{\Lambda}|)$ is now given by substituting (4-1.12) and (4-1.11) into (4-1.14):

$$W(|\vec{\Lambda}|)d|\vec{\Lambda}| = 4\pi|\vec{\Lambda}|^2 W(\Lambda_x)W(\Lambda_y)W(\Lambda_z)d|\vec{\Lambda}|$$

$$(4\text{-}1.15) \quad = |\Lambda|^2 \frac{4\pi}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\vec{\xi}\left[e^{-i\left(\vec{\Lambda}-\sum_j \frac{\vec{\rho}_j}{\rho_j^3}\right)\cdot\vec{\xi}}\right]_{Avg} d|\vec{\Lambda}| \quad ,$$

where

$$d\vec{\xi} \equiv d\xi d\eta d\zeta$$

$$(\vec{\Lambda} - \sum_j \vec{\rho}_j/\rho_j^3)\cdot\vec{\xi} \equiv (\Lambda_x - \sum_j \rho_{jx}/\rho_j^3)\xi + (\Lambda_y - \sum_j \rho_{jy}/\rho_j^3)\eta + (\Lambda_z - \sum_j \rho_{jz}/\rho_j^3)\zeta \quad .$$

This is precisely the integral encountered in the usual Markoff theory. Transforming to polar coordinates yields

$$(4\text{-}1.16) \quad W(|\vec{\Lambda}|)d|\vec{\Lambda}| = \frac{|\vec{\Lambda}|^2}{2\pi^2}\int_0^{\infty}|\vec{\xi}|^2 d|\vec{\xi}|\int_{-1}^{+1} d\mu \int_0^{2\pi} d\phi\, e^{-i|\vec{\Lambda}||\vec{\xi}|\mu}\left(e^{\frac{i\sum\vec{\rho}_j\cdot\vec{\xi}}{\rho_j^3}}\right)_{Avg} d|\vec{\Lambda}| \quad ,$$

where

$$d\vec{\xi} = d\phi\, d\mu\, |\vec{\xi}|^2\, d|\vec{\xi}| \quad ,$$

and integrating over the angles gives

$$(4\text{-}1.17) \quad W(|\vec{\Lambda}|)d|\vec{\Lambda}| = \frac{2}{\pi}|\vec{\Lambda}|\int_0^{\infty}\xi\, d\xi \sin|\vec{\Lambda}|\xi\left(e^{i\sum_j \vec{\rho}_j\cdot\vec{\xi}/\rho_j^3}\right)_{Avg} d|\vec{\Lambda}| \quad .$$

The static phase

$$(4\text{-}1.18) \qquad i\sum_j \frac{\vec{\rho}_j\cdot\vec{\xi}}{\rho_j^3} = i\sum_j |\vec{\rho}_j|\,\xi\,\mu_j/\rho_j^3 = i\sum_j \frac{\xi\mu_j}{\rho_j^2}$$

is now a scalar sum and can be averaged according to our general formula (3-12.17) for the average phase arising from scalarly additive time-independent perturbations:

$$(4\text{-}1.19)\quad \left(e^{i\sum_j \xi\,\mu_j/\rho_j^2}\right)_{\text{Avg}} = e^{4\pi N\int_0^\infty \rho_j^2\,d\rho_j\int_{-1}^{+1}\frac{d\mu_j}{2}\left(e^{i\xi\mu_j/\rho_j^2}-1\right)},$$

where the variable σ_j in (3-12.17) is the direction cosine μ_j in this application. The angular integration gives for the argument of the exponential,

$$(4\text{-}1.20a)\qquad -4\pi N\int_0^\infty \rho_j^2\,d\rho_j\left(\frac{1-\sin\xi/\rho_j^2}{\xi/\rho_j^2}\right)\quad;$$

with $x \equiv \xi/\rho_j^2$, (4-1.20a) becomes

$$(4\text{-}1.20b)\qquad -2\pi N\xi^{3/2}\int_0^\infty \frac{dx}{x^{5/2}}\left(1-\frac{\sin x}{x}\right).$$

Integration by parts gives the final result:

$$(4\text{-}1.20c)\qquad -\frac{16}{15}\frac{\pi^{3/2}}{2^{1/2}}N\,\xi^{3/2} = 4.21\,\xi^{3/2}N\,.$$

The distribution function is now

$$(4\text{-}1.21)\qquad W(|\vec{\Lambda}|)\,d|\vec{\Lambda}| = \frac{2}{\pi}|\vec{\Lambda}|\,d|\vec{\Lambda}|\int_0^\infty \xi\,d\xi\,\sin|\vec{\Lambda}|\xi\,e^{-4.21\,N\xi^{3/2}}\,.$$

Another convenient form for this integral is found by putting $\xi \equiv AX_{a\alpha}\,y$, then

$$(4\text{-}1.22)\qquad 4.21\,\xi^{3/2}N = 4.21\,(AX_{a\alpha}y)^{3/2}N\,,$$

and defining a new constant $\lambda_{a\alpha}$,

$$(4\text{-}1.23)\qquad \lambda_{a\alpha}^{3/2} \equiv 4.21\,(AX_{a\alpha})^{3/2}N$$

$$\lambda_{a\alpha} = 2.61\,AX_{a\alpha}\,N^{2/3} = 4.52\,X_{a\alpha}\,N^{2/3}\,,$$

the absorption coefficient is now

$$(4\text{-}1.24)\qquad I_{a\alpha}(\Delta\omega_{a\alpha})d\Delta\omega_{a\alpha} = |\mu_{a\alpha}^o|^2\,\frac{2}{\pi}\,\Delta\omega_{a\alpha}^o\int_0^\infty dy\cdot y\,\sin\Delta\omega_{a\alpha}y e^{-(\lambda_{a\alpha}y)^{3/2}}\,d\Delta\omega_{a\alpha}^o\,.$$

Integrals of this type will also be obtained as a special case of formulas in Chapter V, so only the results of the integration will be given in this section. Defining a new dimensionless variable

$$\beta \equiv \frac{\Delta\omega^{o}_{a\alpha}}{\lambda_{a\alpha}} \quad , \tag{4-1.25}$$

the Holtsmark statistical theory yields the following series expansions:

$$W(\beta)d\beta = \frac{I_{a\alpha}(\beta)d\beta}{|\mu^{o}_{a\alpha}|^2} = \frac{4}{3\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{(n-1)!}\Gamma\left[\frac{2}{3}(n+1)\right]\beta^n \sin(n-1)\frac{\pi}{2} \qquad \beta \ll 1$$

(4-1.26)

$$= \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\Gamma\left(\frac{3n+1}{2}\right)\frac{1}{\beta^{\frac{3n-1}{2}}}\sin(3n+1)\pi/4 \qquad \beta \gg 1 \quad .$$

The numerical consequences of these equations have received adequate discussion elsewhere, so we will close our discussion of the mathematics connected with the Holtsmark theory at this point and compare the experimental observations with the theory.

2. Comparison of the Holtsmark Theory with Observation

Turner[1,2] and Doherty[2] compared experimental profiles of H_β obtained with the Michigan shock tube with the Holtsmark theory and also with a profile obtained by Griem[11] with the water-stabilized arc. The temperature in these experiments was about 12,000°K. Figure 4 shows the results.* The ion densities were determined in the shock-tube experiments from measurements of the shock velocity with a rotating-drum camera. The theory predicts that on the wing the intensity is inversely proportional to $\Delta\omega^{5/2}$. The observed intensity on the wings, however, is $(\Delta\omega)^p$, where p is definitely less than 2.5. The measurements indicated that the intensity on the

*Private communication with E. B. Turner and L. Doherty.

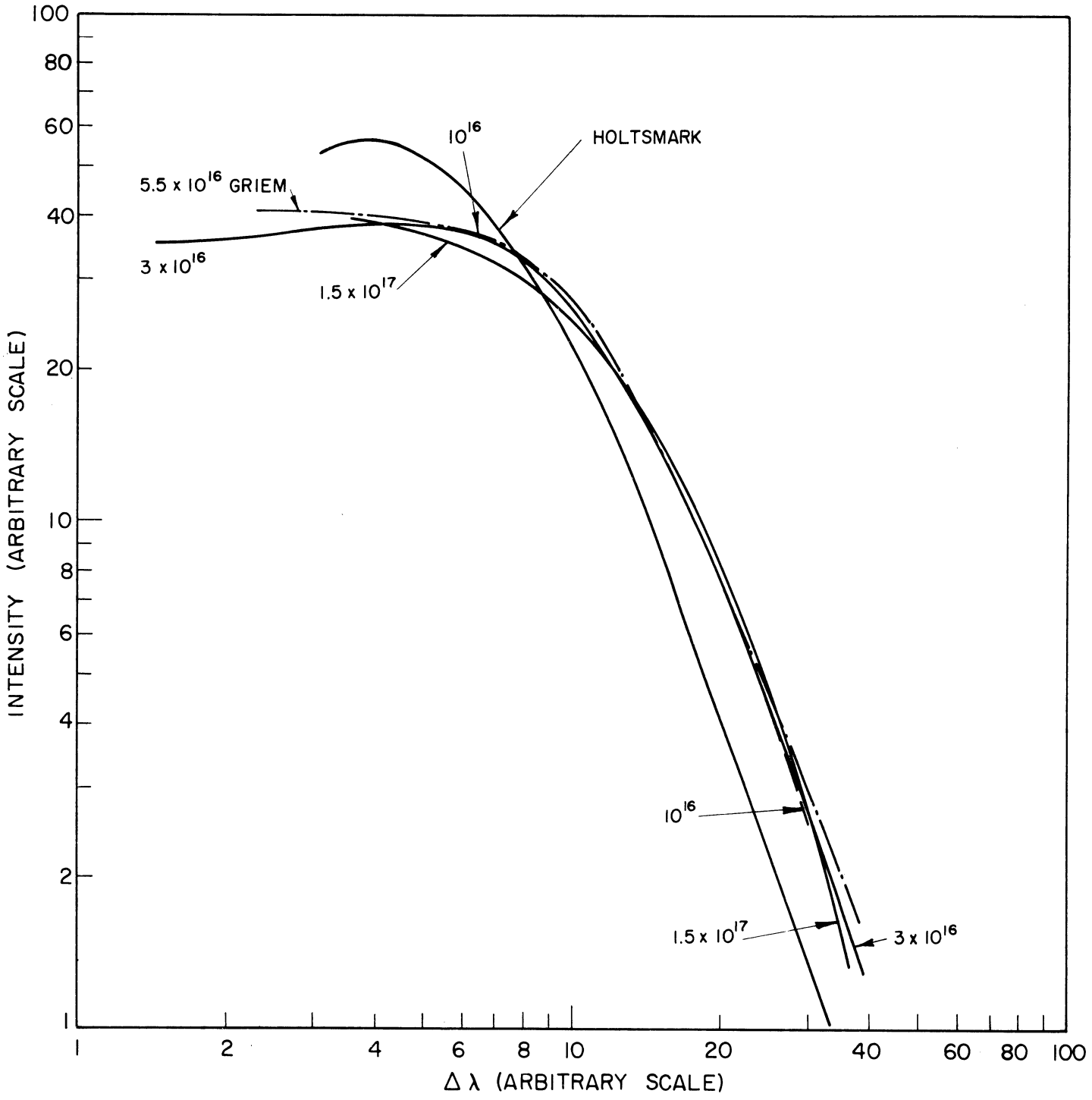


Figure 4. Comparison of shock-tube and arc spectra of H_β with the Holtsmark distribution (log-log plot).

wings did not drop off as rapidly as the Holtsmark theory predicted. It should also be noted that the line shapes determined in the water-stabilized arc and in the shock tube agree closely with one another on the wing. Griem's photometry was more accurate than the time-resolved shock-tube spectra because longer exposures could be made with the arc. The shock tube has the advantage that the ion density can be determined independently from hydrodynamic calculations and that the radiation is produced in a homogeneous region so that no corrections for temperature gradients are necessary.

The qualitative conclusions drawn from these data are that there is about a 20-percent discrepancy between the observed half-width and the Holtsmark half-width and that there is approximately a factor of two between the measured and Holtsmark wing intensities over the frequency range observed.

The laboratory data are also consistent with astrophysical observations. Since Struve[52] and Elvey[53] recognized in 1929 that the Stark effect plays an important role in the broadening of hydrogen lines in stellar atmospheres, a great number of data have been accumulated and interpreted according to the Holtsmark theroy. The general impression that one gets from this work is that the densities, temperatures, and surface gravities derived from the observed profiles using the Holtsmark theory and the general theory of radiative transfer are inconsistent with those derived from the continuous-spectra, metallic line intensities and also masses and radii of components of eclipsing binaries. It appears that the observed widths of the Balmer lines are greater than predicted by the statistical theory, which can treat only the broadening by ions. It has been suggested by Odgers[54] that electron broadening as well as ion broadening

might account for the extremely wide hydrogen lines (200Å) observed in A-type stars. Miss Underhill[55] also finds that the Holtsmark theory seems to yield too narrow a profile for H_γ in the O-type stars σ Orionis and 10 Lacertae. Similar conclusions were reached by Aller[56] and Miss McDonald[57] in connection with their studies of type-B stars. The hydrogen lines observed in the solar spectrum are also wider than is predicted by the statistical theory. This list is incomplete and serves only to illustrate that the Holtsmark theory seems to be inadequate for a description of hydrogen line profiles in high-temperature atmospheres. The astrophysical observations must, of course, be viewed with caution since some mechanism other than collision broadening (in the general sense) might be responsible for the wide hydrogen lines. Thus, de Jager[58] has suggested that the additional broadening of the solar Balmer lines might be due to microturbulence in the solar photosphere. He found that the temperature fluctuations necessary to reproduce the observed profiles must be of the order ± 1000°K. However, the astrophysical evidence coupled with data obtained from shock tubes and arcs strongly suggests that certain modifications to the Holtsmark theory are necessary.

3. The Krogdahl Theory

The Holtsmark statistical theory follows as a special case of the adiabatic approximation to the classical path theory of line broadening. The perturbation is taken to be time independent in the statistical limit so that the motion of the ions is completely neglected. Therefore, according to the Holstein inequality, the theory is not applicable near the line center. Mrs. Krogdahl[59] sought to modify the Holtsmark distribution by taking into account the motion of the ions. For scalarly additive time-dependent perturbations, the formula (3-10.5) for the absorption coeffi-

cient with the average phase (3-12.12) may be employed to calculate the line profile. The integrals involved are perfectly definite and can be done numerically in the intermediate range of frequencies where neither the statistical nor the phase-shift approximations are strictly valid. A method for carrying out these integrations was described by Lindholm[44] and improved recently by Anderson.[60] However, for vectorially additive time-dependent perturbations of the type encountered in the Stark broadening of the Balmer lines by electric fields, the average phase (3-11.12) derived for scalarly additive perturbations is not applicable.

Mrs. Krogdahl argued as follows:[59] "... since the perturbations are to be added vectorially we must regard the frequency ω as a vector as well as the quantity t [time], as used in evaluating the phase shift. While at first sight it may seem somewhat artificial to regard time and frequency is vectors, it must be remembered that the quantity t, as it occurs here, is really derived from the trajectory, which is a directed quantity dependent on the time. Likewise frequency differences are always proportional to differences of momenta ..."

The absorption coefficient (3-10.5) was then written

$$(4\text{-}3.1)\quad I_{a\alpha}(\Delta\vec{\omega}^{o}_{a\alpha}) = |\mu^{o}_{a\alpha}|^2 \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} d\vec{t}\; e^{-i\Delta\vec{\omega}^{o}_{a\alpha}\cdot\vec{t}}\left[e^{\,i\int_{o}^{t}(\Delta\vec{\omega}_a-\Delta\vec{\omega}_\alpha)\cdot d\vec{t}}\right]_{Avg}$$

and the distribution $I_{a\alpha}(\Delta\omega^{o}_{a\alpha})$ was found from

$$(4\text{-}3.2)\quad I_{a\alpha}(\Delta\omega^{o}_{a\alpha})\, d\Delta\omega^{o}_{a\alpha} = [4\pi(\Delta\omega^{o}_{a\alpha})^2\, d\Delta\omega^{o}_{a\alpha}]\, I_{a\alpha}(\Delta\vec{\omega}^{o}_{a\alpha}) \quad ,$$

where

$$d\Delta\vec{\omega}^{o}_{a\alpha} = 4\pi(\Delta\omega^{o}_{a\alpha})^2\, d\Delta\omega^{o}_{a\alpha} \quad ; \quad \Delta\omega^{o}_{a\alpha} \equiv |\Delta\vec{\omega}^{o}_{a\alpha}| \quad .$$

The numerical calculations of Mrs. Krogdahl were based on these formulas

and followed the integrating scheme of Lindholm.[44] She has found that the corrections to the Holtsmark theory obtained in this way were generally quite small and certainly could not account for the observed discrepancy between the experimental data and the Holtsmark theory.

The argument that the frequency and time must be taken as vectors for vectorially additive perturbations because trajectories and momenta differences are involved is not self-evident. In this section it will be shown that the Krogdahl formula follows from statistical assumptions and is not connected with momenta changes or pertuber trajectories. However, we have not yet been able to justify these assumptions from first principles.*

The basic expression for the absorption coefficient in the adiabatic limit is again

$$(3\text{-}10.5)\quad I_{a\alpha}(\omega)d\omega = |\mu^{o}_{a\alpha}|^2 \frac{d\omega}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{\,i\int_0^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt} \right]_{Avg} ,$$

where the time-dependent phase for the first-order Stark effect is

$$(4\text{-}3.3)\qquad \int_0^{\tau} (\Delta\omega_a - \Delta\omega_\alpha)dt = AX_{a\alpha} \int_0^{\tau} \left| \sum_{jk} \frac{r_j(t-t_k)}{r_j^3(t-t_k)} \right| dt \quad .$$

The notation here is the same as in the previous section pertaining to the Holtsmark theory for time-independent perturbations. Letting $z \equiv AX_{a\alpha}\tau$ and using (4-3.3), $I_{a\alpha}(\omega)$ becomes

$$(4\text{-}3.4)\quad I_{a\alpha}(\omega)d\omega = \frac{|\mu^{o}_{a\alpha}|^2}{AX_{a\alpha}} \frac{d\omega}{2\pi} \int_{-\infty}^{\infty} dz \left[e^{-i\left(\frac{\Delta\omega^{o}_{a\alpha}}{AX_{a\alpha}} z - \int_0^{z/AX_{a\alpha}} \left| \sum_{jk} r_j/r_j^3 \right| dt \right)} \right]_{Avg} .$$

Let us now define a vector $\vec{\Lambda}(\tau)$ whose absolute magnitude is a constant (but whose direction is time dependent):

*A preliminary report on this phase of the work was given at the Stellar Atmospheres Conference, Indiana Univ., Oct, 1954, and before the Astronomical Society, April, 1955, Ref. 31.

$$(4\text{-}3.5) \qquad |\vec{\Lambda}(\tau)| \equiv \frac{\Delta\omega^{o}_{a\alpha}}{AX_{a\alpha}} \quad .$$

The direction of $\vec{\Lambda}(\tau)$ is taken to be in the direction of the instantaneous electric field,

$$(4\text{-}3.6) \qquad \vec{\Lambda} \cdot \sum_{jk} \vec{r}_j/r_j^3 = \frac{\Delta\omega^{o}_{a\alpha}}{AX_{a\alpha}} \left| \sum_{jk} \vec{r}_j/r_j^3 \right| \quad ;$$

with this substitution in (3-10.5), the following result is obtained:

$$(4\text{-}3.7) \quad I_{a\alpha}(\omega)d\omega = I_{a\alpha}(\Delta\omega^{o}_{a\alpha})d\Delta\omega^{o}_{a\alpha} = AX_{a\alpha}\, I_{a\alpha}\,(|\vec{\Lambda}|)\, d|\vec{\Lambda}|$$

$$I_{a\alpha}(|\vec{\Lambda}|)\, d|\vec{\Lambda}| = |\mu^{o}_{a\alpha}|^2 \frac{d|\vec{\Lambda}|}{2\pi} \int_{-\infty}^{\infty} d\xi \left(e^{-i\left|\vec{\Lambda} - \int_0^{z/AX_{a\alpha}} \sum_{jk} r_j/r_j^3\, dt\right| z} \right)_{Avg}$$

$$\equiv |\mu^{o}_{a\alpha}|^2 W|\vec{\Lambda}|\, d|\vec{\Lambda}| \quad .$$

In obtaining (4-3.7) no assumptions were necessary. The only mathematical operation involved was a simple transformation of variables by introducing the auxiliary vector $\vec{\Lambda}(\tau)$. Since we have chosen $\vec{\Lambda}$ to be in the same direction as the instantaneous electric field, the x, y, and z components of $\vec{\Lambda}$ are directly proportional to the x, y, and z components of the instantaneous electric field strength, respectively. To obtain the Krogdahl formula, it is necessary to assume that the probability distribution of a component of $\vec{\Lambda}$, say Λ_x, is given by

$$(4\text{-}3.8) \quad W(\Lambda_x)d\Lambda_x = \frac{d\Lambda_x}{2\pi} \int_{-\infty}^{\infty} d\xi \left\{ e^{-i\left[\Lambda_x - \int_0^{\xi/AX_{a\alpha}} \left(\sum_{jk} \vec{r}_j/r_j^3\right)_x d\xi'\right]\xi} \right\}_{Avg} ,$$

and that the distribution of $\vec{\Lambda}$ is given by the product

$$(4\text{-}3.9) \quad W(\vec{\Lambda})\vec{d\Lambda} = W(\Lambda_x)W\Lambda_y)W(\Lambda_z)d\Lambda_x d\Lambda_y d\Lambda_z = 4\pi|\vec{\Lambda}|^2\, d|\vec{\Lambda}|\, W(\Lambda_x)W(\Lambda_y)W(\Lambda_z) \quad .$$

Then by exactly the same methods used in the previous section one obtains the Krogdahl formula (4-3.1). In the static limit, where $\vec{\Lambda}(\tau)$ has a fixed direction, this formula reduces to the exact Holtsmark distribution. For time-dependent fields it is not clear that the probability distribution of the x, y, and z components of $\vec{\Lambda}$ is statistically independent so that the product distribution (4-3.9) can be justified. Because of this uncertainty, the modifications of the Holtsmark theory derived with (4-3.1) and (4-3.2) may not be correct. It appears, therefore, that the refinement of the Holtsmark theory to take into account simultaneously the motion of the ions and multiple interactions remains to be done.

4. Spitzer's Theory of Lyman α

In Section III.14 it was demonstrated that the weak collision theory leads as a special case to a formula given by Spitzer[9] for describing the Lyman α line. The averaging procedure employed by Spitzer was based on the assumption of binary collisions. The difficulties inherent in the Krogdahl formula are thereby avoided since the vector addition of the electric fields of several ions does not enter into the problem if only binary collisions are considered.

The numerical analysis contained in Spitzer's work showed a gradual transition between the Holtsmark statistical distribution valid on the wing of the line to a Weisskopf[61] type impact distribution valid for the line center. It was also stated by Spitzer that the broadening due to fast electrons can be neglected, in general, in comparison with the broadening due to an equal density of the slow-moving ions. This assertion will be re-examined in connection with our work and also that of Griem.[11] The Spitzer theory included an effect due to the rotation of the coordinate system whose z-axis points in the direction of the passing ion. In the

usual theory of the Stark effect, the z-axis is chosen to be in the direction of the external static electric field. The radiation field and transition matrix elements are then described with respect to the same space-fixed coordinate system. For the time-dependent electric field due to a moving ion, the matrix elements calculated with respect to the space-fixed coordinate system used to describe the radiation have an additional time dependence due to the rotation of the z-axis. For the long-range, weak interactions which are important near the line core, Spitzer showed that the electronic quantum states doe not adiabatically "follow" the rapidly rotating field and that each distant collision produces a phase change of π in the radiation. Spitzer showed that this rotation effect can be taken into account in a careful analysis which included a detailed account of all nonadiabatic processes. Furthermore, it was demonstrated that the statistical distribution applies to the line wing and that the rotation effect is not important. In our work only the line wing is considered so that the ions can be treated as if they were stationary. Consequently, the usual theory of the Stark effect can be employed if a coordinate system is chosen to be in the direction of the instantaneous ion field. In treating the fast electrons, the rotation effect is avoided by this choice of a stationary coordinate system determined by the instantaneous ion configuration. This procedure is valid because, according to the Holtsmark theory, the probability of zero ion field is zero. Consequently, the radiating atom always finds itself perturbed by ions. This perturbation removes the normal hydrogen degeneracy and the resulting wavefunctions are given by the usual Stark effect theory. Each electron collision is then considered to produce phase shifts and induce transitions among these non-degenerate states. When the electron broadening is calculated in this way

it is found that it is not negligible compared to the ion broadening. In addition, the binary collision assumption of Spitzer can be completely removed from the theory.

In this connection it should be noted that the Spitzer binary collision theory and the Krogdahl theory lead to completely different distributions in the line center. There could be several reasons for this: (1) the corrections to the Holtsmark theory due to the motion of the ions are important in the line center where the nearest neighbor (binary collision theory employed by Spitzer) approximation also breaks down, and (2) the Krogdahl formula may not be correct for the reasons discussed in the previous section. For these reasons the theory of Balmer line broadening near the line center is very unsatisfactory and we have been unable to improve the situation.

5. Inglis-Teller Theory of Electron Broadening

Inglis and Teller[12] attempted to calculate the manner in which the spectral lines in hydrogen-like spectra merge into a continuum due to Stark broadening. The broadening by both ions and electrons was considered by these authors. However, they indicated that the electron broadening is not as important as the ion broadening. The Holtsmark theory was used in treating the ions, while the electron broadening was found from order-of-magnitude considerations. In our notation, the Inglis-Teller estimate follows from the following argument for distant collisions. According to (3-9.13) the wavefunctions describing the radiating atom in the weak collision approximation are of the form

$$(3\text{-}9.13)\quad \chi_\alpha(t) = \phi_\alpha\, e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} + \sum_\beta{}' C_{\beta\alpha}(t)\, \phi_\beta(t)\, e^{-\frac{i}{\hbar}\int_0^t E_\beta(t')dt'}.$$

The coefficients $C_{\beta\alpha}(t)$ describe the nonadiabatic transitions and the probability that such a transition has occurred is

$$\sum_{\beta}' |C_{\beta\alpha}(t)|^2 \quad . \tag{4-5.1}$$

In the high-velocity limit (phase-shift approximation or "collision" theory in the terminology of Inglis-Teller), using (3-15.4), with $\omega^{o}_{\alpha\beta}=0$, and an inverse-square perturbation, the transition amplitudes are

$$\begin{aligned} |C_{\beta\alpha}(t)|^2 \to |C_{\beta\alpha}(\infty)|^2 &= \left| \int_{-\infty}^{\infty} \frac{[H_1(t')]_{\beta\alpha}}{\hbar}\, dt' \right|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} \frac{A_{\beta\alpha} dt}{(v^2t^2+\rho^2)} \right|^2 \\ &= \frac{1}{\hbar^2} \left| \frac{A_{\beta\alpha}\pi}{\rho\, v} \right|^2 , \end{aligned} \tag{4-5.2}$$

but

$$[H_1(0)]_{\beta\alpha} = \frac{A_{\beta\alpha}}{\rho^2} ,$$

thus

$$|C_{\beta\alpha}(\infty)|^2 = \frac{\rho^2\pi^2}{v^2\hbar^2} |[H_1(0)]_{\beta\alpha}|^2 \quad . \tag{4-5.3}$$

The total transition probability for the nonadiabatic contribution to the broadening is now approximately

$$\sum_{\beta}' |C_{\beta\alpha}(\infty)|^2 = \frac{\rho^2\pi^2}{v^2\hbar^2} \sum_{\beta}' |[H_1(0)]_{\beta\alpha}|^2 \quad . \tag{4-5.4}$$

This expression differs from that of Inglis-Teller in two respects. The factor π^2 does not appear in their argument and their sum over β includes a term $|[H_1(0)]_{\alpha\alpha}|^2$ which does not enter into the nonadiabatic transition probability. It has been shown in Chapter III that the diagonal and nondiagonal matrix elements of the perturbation enter formally into the weak collision theory in an identical fashion. One might say, therefore, that

the phase shifts act like transition probabilities since they cause a transition from an unperturbed wave to a new wave that is out of phase with the original wave. The total transition probability, including transitions to a wave of different phase (that is, the adiabatic as well as the nonadiabatic transitions), is then given by the unprimed sum

$$(4\text{-}5.5) \qquad \left(\frac{\rho\pi}{\hbar v}\right)^2 \sum_{\beta} |[H_1(0)]_{\beta\alpha}|^2 = \left(\frac{\rho\pi}{\hbar v}\right)^2 [H_1^2(0)]_{\alpha\alpha} \ .$$

Now except for the factor π^2, this is the expression obtained in the Inglis-Teller paper. However, their argument that for distant collisions there are two regions in which the broadening is purely adiabatic or purely nonadiabatic is not correct. These two effects cannot be separated in such a simple fashion.

The broadening can now be estimated with (4-5.5). Inglis and Teller take $[H_1^2(0)]_{\alpha\alpha}$ to be of the order

$$(4\text{-}5.6) \qquad [H_1^2(0)]_{\alpha\alpha} \sim \left(\frac{ae^2}{\rho^2}\right)^2 \ ,$$

where a is the Bohr radius. The number of collisions per second with impact parameter between ρ and $\rho+d\rho$ is given by $vN\ 2\pi\rho d\rho$ so that there are

$$(4\text{-}5.7) \qquad (Nv\ 2\pi\rho d\rho)\frac{\rho^2\pi^2}{\hbar^2 v^2}[H_1^2(0)]_{\alpha\alpha} = 2\pi^3 \frac{Na^2e^4}{v\hbar^2}\frac{d\rho}{\rho}$$

transitions per second. The total number of transitions per second is found by integrating from ρ_c to ρ_m, where ρ_c is the critical impact parameter for which the phase shift is unity. For larger phase shifts the weak collision theory fails. The impact parameter ρ_m is a maximum impact parameter which takes screening into account. This will be discussed in the next chapter in some detail. The line width is now found from the uncertainty principle

$$\Delta E \sim \hbar \cdot \text{transition probability}$$

$$= -\frac{2\pi^3 N a^2 e^4}{\hbar v} \ln \rho_c/\rho_m \quad , \tag{4-5.8}$$

which agrees again with Inglis-Teller, except for the factor π^2 or the factor π in $[H_1(0)]_{\alpha\alpha}$. These arguments clearly do not follow in a rigorous fashion from the general weak collision theory since the above quantitative results are based on an order-of-magnitude estimate of the matrix elements of the perturbation. With the availability of relatively good experimental data it is of interest to re-examine the influence of nonadiabatic effects more precisely and to investigate how one should include both ion and electrons simultaneously in a theory that includes the possibility of multiple collisions. It should be remarked here, however, that these improvements are in essential agreement with the order-of-magnitude estimates of the Inglis-Teller theory.

6. A Phase-Shift Theory for Electron Broadening

The astrophysical importance of the theory of hydrogen line broadening for high-temperature, partially ionized gases led Unsöld[10] to consider perturbations due to electrons as well as ions. He applied the adiabatic phase-shift approximation of the Lindholm[44]-Foley[32] type to electron broadening. These results were later used by Griem[11] to interpret the Balmer line profiles obtained with a water-stabilized arc. A brief discussion of Griem's calculations and experiments will follow in the next section.

The use of the adiabatic approximation to the classical path theory for electron broadening as applied by Unsöld suffers from three major defects: (1) the collision-induced (or nonadiabatic) transitions are not considered; (2) the relative direction of the electron-impact parameter

with a space-fixed axis of quantization is neglected; and (3) the average over electron velocities was done by replacing the Maxwell-Boltzmann velocity distribution by a delta function $\delta(v-\bar{v})$, where $\bar{v}$ is the average velocity. It will be shown in Chapter V that all three of those approximations lead to appreciable errors. In order to compare our results with this earlier theory, the Unsöld half-width formula will be derived here as an approximation to the formal theory given in Chapter III.

The interaction in the classical path theory between an electron and a hydrogen atom is given by the diagonal matrix elements of $-(e\vec{r} \cdot \vec{F}_e)$ where $e\vec{r}$ is the dipole moment operator for the radiating hydrogen atom and $\vec{F}_e$ is the instantaneous total electric field of all the individual electron field strengths:

$$\vec{F}_e = \sum_i (\vec{F}_e)_i \quad . \tag{4-6.1}$$

In the Unsöld calculation the interaction was written $H_1(t) = - |e\vec{r}||\vec{F}_e|$, i.e., $\vec{r}$ was taken to be in the direction of $\vec{F}_e$. This approximation is not justified and neglects an important angular dependence in the interaction. The matrix elements of $|e\vec{r}|$ were taken by Unsöld to be those given by the usual Stark effect theory. This approximation neglects completely all non-adiabatic and "rotation" effects. If it is also assumed that only binary collisions are important, then one can write the Hamiltonian $H_1(t)$ as

$$H_1(t) \simeq H_i(t) = - |e\vec{r}| \, |(\vec{F}_e)_i| \quad . \tag{4-6.2}$$

With these assumptions it is now a simple matter to obtain the half-width in the phase-shift approximation. With the notation of Chapter III the phase integral corresponding to the perturbation (4-6.2) is

$$\int_{-\infty}^{\infty} (\Delta\omega_a - \Delta\omega_\alpha)dt \equiv \frac{1}{\hbar} \int_{-\infty}^{\infty} \left\{ [H_i(t)]_{aa} - [H_i(t)]_{\alpha\alpha} \right\}_{dt}$$

$$(4\text{-}6.3) \qquad = AX_{a\alpha} \int_{-\infty}^{\infty} \frac{dt}{v^2 t^2 + \rho_i^2}$$

$$= \frac{AX_{a\alpha}\, \pi}{\rho_i v} \quad .$$

The half-width parameter $\gamma_{a\alpha}$ is found by substituting this phase integral into the expression (3-11.14) with $W(v) = \delta(v-\bar{v})$:

$$(4\text{-}6.4) \qquad \gamma_{a\alpha} = 2\pi N\bar{v} \int_0^{\rho_m} \rho d\rho \left(1 - \cos \frac{AX_{a\alpha}\, \pi}{\rho\, \bar{v}}\right) ,$$

where the integration extends from zero to a maximum impact parameter ρ_m determined by the screening of other ions and electrons (see Chapter V). Letting

$$(4\text{-}6.5) \qquad x \equiv \frac{AX_{a\alpha}\, \pi}{\rho\, \bar{v}}$$

and

$$(4\text{-}6.6) \qquad \frac{AX_{a\alpha}\, \pi}{\bar{v}\, \rho_m} \equiv \delta_m^{a\alpha} ,$$

the half-width parameter $\gamma_{a\alpha}$ becomes

$$(4\text{-}6.7) \qquad \gamma_{a\alpha} = 2\pi^3 \frac{N}{\bar{v}} (AX_{a\alpha})^2 \int_{\delta_m^{a\alpha}}^{\infty} \frac{dx}{x^3} (1 - \cos x) \quad .$$

A partial integration with $\delta_m^{a\alpha} \ll 1$ yields

$$(4\text{-}6.8) \quad \gamma_{a\alpha} = -\pi^3 \frac{N}{\bar{v}} (AX_{a\alpha})^2 \left[0.923 - \ell n\, \delta_m^{a\alpha} + \frac{(\delta_m^{a\alpha})}{24} + \ldots \right] .$$

It is easily verified that the phase change $\delta_m^{a\alpha}$ is small compared to unity

for the inverse-square interaction so that the first two terms in the series expansion give a high degree of accuracy for the integral. The result (4-6.8)is that obtained by Unsöld.[10] According to the theory given in Chapter III, there is also a nonzero shift $\gamma'_{a\alpha}$ in the position of the line center. Unsöld argued that the shift could be neglected since the Stark components are symmetric about the unperturbed line center. This result should follow from the formal analysis. It will be shown (Chapter V) that the shift is in fact zero in the adiabatic approximation if the angular dependence in the interaction is taken into account. It is therefore unnecessary to take $\gamma'_{a\alpha}$ to be zero in an ad hoc fashion. It will also be shown that the binary collision assumption is not necessary in treating electron broadening.

7. Griem's Theory for Hydrogen Line Broadening by Ions and Electrons

Discrepancies between Balmer line profiles determined experimentally (with a water-stabilized arc) and those predicted by the Holtsmark theory for ions led Griem[11] to investigate further the effect of electron collisions on these profiles. His calculations were based on the half-width parameter obtained by Unsöld (previous section) with the adiabatic phase-shift approximation. Griem recognized that the nonadiabatic transitions and the Spitzer rotation effect* (see the discussion in Section IV.4) are not taken into account in the Unsold[10]-Lindholm[44] theory. An approximate (ad hoc) procedure for taking nonadiabatic effects into account for degenerate systems is to apply the adiabatic formula for the nondegenerate case with an interaction derived from an unweighted average of the Stark dis-

*Neglecting the "rotation effect" of Spitzer is equivalent to neglecting the angular dependence of the perturbation Hamiltonian discussed in Section 6 of this chapter.

placements in a homogeneous static electric field. This method tended to overestimate the electron broadening* but reduced considerably the discrepancy between the theory and experiment. Our theoretical development is essentially an attempt to calculate the phase-shift and nonadiabatic contributions to the line shape in a more rigorous fashion. The results will also be compared with the estimates of Inglis and Teller[12] in the next chapter.

It should be remarked also that Griem treated the ions in the statistical or static field approximation. It follows from the Holstein inequality[47] that this approximation should be quite accurate for the Balmer line wings and is also used in our analysis. Griem was also concerned with the justification of the binary collision approximation. He indicated that since the close collisions are the most important in determining the perturbation field, the more distant collisions may be neglected. This conclusion is not supported by our work, where it will be shown that the main contribution to the collision cross section arises from distant collisions for inverse-square interactions. When one considers long-range interactions, multiple collisions might be important. It was found (Chapter V) that it is possible to include long-range multiple electron collisions in the theory without difficulty. The results are exactly the same as for the binary collision approximation. Because of this fact, the limiting density derived by Griem at which multiple electron collisions become important is not a fundamental limitation of the theory.

8. Summary

The Holtsmark theory for hydrogen line broadening due to ion perturbations is valid on the Balmer line wings where the Holstein inequality

*Private communication with H. Griem.

is satisfied. This conclusion is also supported by the work of Spitzer, who considered deviations from the statistical theory. The correction terms obtained by Mrs. Krogdahl are questionable because the Fourier integral used in her work cannot be shown to be rigorously justified. A theory that takes into account multiple collisions in the line center, where neither the statistical nor the high-velocity approximations hold, is still to be desired.

The theory of electron broadening can also be improved in several ways. For long-range interactions where the binary collisions approximation might fail, it is of some interest to investigate the effect of multiple collisions. This calculation will involve the consideration of the relative direction of the electrons and the direction of the instantaneous static electric field due to the ions. One can also take into account nonadiabatic effects in these calculations. There is also the question of what line shift is to be expected due to electron collisions. This point was not considered by Inglis and Teller and was not discussed in a quantitative fashion by Unsöld. Furthermore, none of these theories averages properly the electron velocities over a Maxwellian distribution. In addition, the existing theories in the classical path approximation contain only order-of-magnitude estimates of the various matrix elements involved. Consideration of these factors will be the main concern of the next chapter.

CHAPTER V

HYDROGEN LINE BROADENING BY IONS AND ELECTRONS

1. Introduction

In Chapters III and IV the formal theory of line broadening in the classical path approximation was discussed and compared qualitatively with the results of others. In this chapter the theory will be applied quantitatively to the problem of hydrogen line broadening in a partially ionized gas. Particular attention will be given to the Lyman α line ($n = 1 \rightarrow 2$) 1216Å since it has a relatively simple structure and also because it has already received much attention in the literature. This detailed study of Lyman α will serve to illustrate the main features of the theory as a guide for the calculation of the profiles of the Balmer lines which have a more complicated structure but for which experimental data are available.

Before discussing Lyman α in detail, however, the validity of the approximations used for both ion and electron broadening will be first examined on the basis of the Spitzer[9]-Holstein[47] inequality. The adiabatic contribution (involving the diagonal matrix elements of the perturbation) to the electron broadening will then be presented together with a discussion of the Debye screening length. These results will next be compared with the adiabatic theory of Lindholm[44] and Foley[32] as applied by Unsöld[10] and Griem[11] to the first-order Stark broadening of hydrogen due to electron collisions.

The section concerned with Lyman α will include both adiabatic and nonadiabatic effects and a comparison of the numerical results with the

work of Spitzer,[9] Inglis-Teller,[12] and the recent quantum theory of electron broadening due to Kivel, Bloom, and Margenau.[15] The classical path and quantum theories will be shown to be equivalent. This lends support to the arguments in Chapter III which were intended to justify the use of the classical path approximation in the theory of hydrogen line broadening by ions and electrons.

The remainder of the chapter will be devoted to some approximate procedures for calculating Balmer line shapes when both "static" ions and "fast" electrons are responsible for the broadening. This phase of the investigation has not yet been completed due to the large amount of numerical analysis involved. The results obtained so far will be compared with experimental Balmer line profiles obtained in the University of Michigan shock tube by Turner[1,2] and Doherty.[2] Suggestions for future calculations will also be outlined briefly.

2. Consequences of the Spitzer-Holstein Inequality

In Sections III.12 and III.13 the Spitzer-Holstein inequality, which expresses the validity range of the phase-shift and statistical theories, was obtained by expanding the phase integral in powers of the velocities $1/v$ and v, respectively. It was found that the statistical theory is valid if the perturbers moved slowly enough so that the duration of a collision is long compared to the times ($\Delta\tau \sim 1/\Delta\omega$) that contribute to the Fourier integral expression for the line shape. The phase-shift approximation, on the other hand, may be used if the perturbers move so fast that the duration of each collision is small compared to $\Delta\tau$. In that case each interaction behaves like a delta function in time and the phase integral can be replaced by the total phase change per collision. Both the statistical and phase-shift approximations allow great simplifications to be made in

the theory, as was indicated in Chapters III and IV. Fortunately, these approximations turn out to be excellent for many applications to the study of high-temperature phenomena.

According to the Spitzer-Holstein inequality, the statistical theory is valid for frequencies satisfying the relation (see 3-12.8 and 3-13.9)

$$(5\text{-}2.1) \qquad \Delta\omega \gg \frac{v^2}{AX_{a\alpha}} \equiv \Delta\omega_c \quad ,$$

where the perturbation behaves like $AX_{a\alpha}/r^2$ for the first-order Stark broadening of hydrogen. The strength of the interaction, $AX_{a\alpha}$, is given by (4-1.6). The phase-shift approximation can be used when the above inequality is reversed according to (3-13.9).

In Table I the $X_{a\alpha}$ are tabulated for the Stark components of the Balmer lines H_α, H_β, H_γ, and H_δ, together with the relative f-numbers, $f_{a\alpha}$, which are proportional to the frequency $\omega^o_{a\alpha}$ and the dipole matrix elements $|\mu^o_{a\alpha}|^2$. These f-numbers were taken from the work of Schrödinger[62] and include a factor of two which takes into account both the x and y matrix elements for the perpendicular radiation (σ components). This factor of two was not included in the early calculations of Verweij,[6] who applied the Holtsmark theory to the Balmer lines of hydrogen. With these values of $X_{a\alpha}$ one can now readily determine the frequencies and temperatures for which the statistical and phase-shift-type theories are applicable. In Table II we have tabulated $\Delta\lambda_c$ for H_β. $\Delta\lambda_c$ is defined by the relation

$$(5\text{-}2.2) \qquad \Delta\lambda_c = \frac{\Delta\omega_c\lambda^2}{2\pi c} = \frac{v^2}{AX_{a\alpha}} \cdot \frac{\lambda^2}{2\pi c} \quad .$$

The broadening is assumed to be due to electrons and ions so that v is taken to be the average electron and proton velocity in a center-of-mass system with respect to a radiating hydrogen atom.

TABLE I

BALMER LINE f-NUMBERS AND STARK DISPLACEMENT COEFFICIENTS

H_α		H_β		H_γ		H_δ	
$X_{a\alpha}$	$f_{a\alpha}$	$X_{a\alpha}$	$f_{a\alpha}$	$X_{a\alpha}$	$f_{a\alpha}$	$X_{a\alpha}$	$f_{a\alpha}$
8	1	12	16	22	7	32	2
6	36	10	373	20	80	30	18
5	32	8	384	18	1318	28	242
4	1618	6	669	17	52	26	10
3	2304	4	912	15	1152	24	180
2	729	2	153	13	1664	22	250
1	3872			12	166	20	18
0	5490			10	1760	18	198
				8	15	16	18
				7	116	14	4
				5	192	12	72
				3	932	10	196
				2	156	8	32
				0	1416	6	396
						4	8
						2	36

TABLE II

$\Delta\lambda_c/T$ FOR THE BALMER LINE H_β

$X_{a\alpha}$	$\frac{\Delta\lambda_c}{T}$ (electrons)	$\frac{\Delta\lambda_c}{T}$ (ions)
2	.21 Å $(°K)^{-1}$	$.23 \times 10^{-3}$ Å $(°K)^{-1}$
4	.11	$.12 \times 10^{-3}$
6	.070	$.076 \times 10^{-3}$
8	.053	$.058 \times 10^{-3}$
10	.042	$.046 \times 10^{-3}$
12	.035	$.038 \times 10^{-3}$

In Table II it can be seen immediately that for temperatures in the range 10,000°K $\Delta\lambda_c$ ranges from 2100 Å to 350 Å for electrons and from 2.3 Å to .38 Å for ions. For Balmer lines of the order 10-200 Å wide (which are observed in spectra from the shock tube and from stellar envelopes) one may apply the statistical theory for the ions and the phase-shift approximation for the electrons, except in the line center and far wings of the lines. For temperatures much greater than 10^4°K the statistical theory cannot be used to describe the ion broadening near the line core. For Lyman α (1216 Å), a line with which we will be concerned later, there are two displaced components (for which $X_{a\alpha} = \pm 2$) and two undisplaced components. For the displaced components $\Delta\lambda_c$ = 120 Å and 0.14 Å for the electrons and protons, respectively.

If the ions which are responsible for the line broadening are not protons but heavier ions, then $(\Delta\lambda_c)_{ions} = \frac{M_p}{M_i} (\Delta\lambda_c)_{protons}$ where M_p and M_i are the reduced masses of the protons and ions interacting with a hydrogen atom of mass m_h:

$$M_p = \frac{m_p m_h}{m_p+m_h} \sim \frac{m_p}{2} \quad (m_h \sim m_p)$$

(5-2.4)

$$M_i = \frac{m_i m_h}{m_i+m_p} \quad ,$$

where $m_i = Am_p$ is the ion mass and m_p is the proton mass. If A, the mass number, is large compared to unity,

$$M_i = \frac{Am_p^2}{(A+1)m_p} \sim m_p \quad . \tag{5-2.5}$$

Then

$$(\Delta\lambda_c)_{ions} = \frac{(\Delta\lambda_c)_{protons}}{2} \quad . \tag{5-2.6}$$

The statistical theory is therefore valid for somewhat smaller frequencies if the broadening is due to electrons and heavy ions instead of electrons and protons. This is of some interest since shock-tube experiments on hydrogen line broadening can be performed in which the ions responsible for the broadening are mainly heavy rare-gas ions.*

From the considerations of this section one may conclude that since the Balmer line wings receive their greatest contribution from the displaced Stark components with large $X_{a\alpha}$, the statistical theory may be used for the ions to describe the line wings. In the remainder of this chapter we will be mainly concerned with how the electron collisions tend to modify the theoretical Holtsmark distribution for static ion fields. It will be seen that the electron broadening is in general not negligible compared to the usual Holtsmark ion broadening.

3. Electron Broadening in the Adiabatic Approximation

In the theory under discussion here the broadening of hydrogen lines due to collisions between fast electrons and radiating hydrogen atoms in a high-temperature plasma is considered to arise from two effects. The passing electron can (1) cause a phase change in the atomic wavefunctions or (2) induce transitions among the normally degenerate substates of the unperturbed hydrogen atom. The first effect is characteristic of the usual phase-shift theory for a two-state (nondegenerate) atom and will be referred to as the adiabatic broadening. The broadening which arises from collision-induced transitions will be referred to as nonadiabatic broadening. It will be seen later that these two broadening mechanisms are es-

*Hydrogen can be introduced into the shock tube as an impurity with a rare gas so that there is a relatively low proton density. Also, in the photosphere of the sun the ions come mainly from metals with a lower ionization potential than hydrogen.

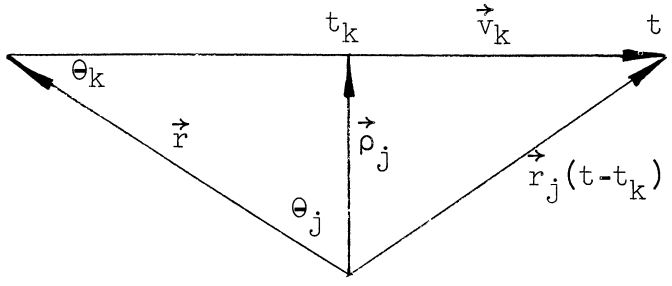
sentially incoherent processes and do not interfere with one another. It is therefore convenient to discuss first the adiabatic broadening (which involves only the diagonal matrix elements of the perturbation Hamiltonian). The analysis of the adiabatic broadening is quite similar to the nonadiabatic analysis, so it is instructive to consider first the simple case in which collision-induced transitions are neglected. The analysis of Lyman α in following sections indicates the method of including both adiabatic and nonadiabatic electron broadening in the theory.

The electric field of the electrons in a plasma can interact with a radiating atom causing phase shifts and transitions among the degenerate substates. The dipole interaction is given by

$$(5\text{-}3.1) \qquad H_1(t) = e\vec{r} \cdot \vec{F}_e(t) = \sum_{jk} e\vec{r} \cdot e \frac{\vec{r}_j\,(t-t_k)}{[r_j(t-t_k)]^3} \quad ,$$

where $e\vec{r}$ is the dipole moment operator of the radiating atom defined with respect to a space-fixed coordinate system and $\vec{r}_j(t-t_k)$ is a vector describing the position of a passing electron with time of closest approach t_k and impact parameter ρ_j.

GEOMETRY OF A COLLISION



The vector $\vec{r}_j(t-t_k)$ can be expressed in terms of $\vec{v}_k$ and $\vec{\rho}_j$:

$$(5\text{-}3.2) \qquad \vec{r}_j(t-t_k) = \vec{\rho}_j + (t-t_k)\,\vec{v}_k \quad .$$

Let $\mu_j \equiv \cos\theta_j$ and $\mu_k \equiv \cos\theta_k$ be the direction cosines defined by the vectors $(\vec{r},\vec{\rho}_j)$ and $(\vec{r}, \vec{v}_k)$. The interaction (5-3.1) can be written with (5-3.2) in terms of μ_j and μ_k:

$$H_1(t) = \sum_{kj} \frac{e^2 r}{[v_k^2(t-t_k)^2 + \rho_j^2]^{3/2}} [\rho_j\mu_j + v_k\mu_k(t-t_k)]$$

(5-3.3)

$$= \sum_{jk} \frac{e^2 r}{(v_k^2x^2 + \rho_j^2)^{3/2}} (\rho_j\mu_j + v_k\mu_k\, x) \quad ,$$

where $t-t_k \equiv x$. In the phase-shift approximation it was shown in Section III.13 that the integrals

$$\int_o^t H_1(t)\, dt$$

can be replaced by integrals from $-\infty \to \infty$:

$$\int_o^t H_1(t)dt \to \int_{-\infty}^{\infty} H_1(x)dx = \sum_{kj} e^2 r\rho_j\mu_j \int_{-\infty}^{\infty} \frac{dx}{(v_k^2x^2 + \rho_j^2)^{3/2}}$$

(5-3.4)

$$= \sum_{kj} e^2 r\rho_j\mu_j \frac{2}{v_k\rho_j^2} \quad .$$

The term involving

(5-3.5)
$$\int_{-\infty}^{\infty} \frac{xdx}{(v_k^2\, x^2 + \rho_j^2)^{3/2}} = 0$$

vanishes.

The phase change per collision is found from the diagonal matrix elements of (5-3.4):

$$\int_{-\infty}^{\infty} (\Delta\omega_a - \Delta\omega_\alpha)dt = \int_{-\infty}^{\infty} [(H_1)_{aa} - (H_1)_{\alpha\alpha}] \frac{dt}{\hbar}$$

(5-3.6)

$$= \sum_{kj} \frac{2e^2}{\rho_j v_k \hbar} [(\phi_a r\mu_j\phi_a) - (\phi_\alpha, r\mu_j\phi_\alpha)] \quad .$$

Now $\mu_j = \cos \Theta_j$ is the direction cosine between the directions defined by $\vec{r}$ and $\vec{\rho}_j$. This direction cosine can be expressed in terms of the polar angles (Θ,ϕ) and (Θ_j,ϕ_j), which describe the orientation of $\vec{r}$ and $\vec{\rho}_j$ with respect to some space-fixed coordinate system. The atomic coordinates are r, Θ, and ϕ, while Θ_j and ϕ_j are coordinates which describe the position of the moving electron relative to the radiator. It will be necessary to perform a statistical average over these collision angles Θ_j and ϕ_j. According to the rules of spherical trigonometry, μ_j is related to Θ, ϕ, Θ_j, and ϕ_j by the relation

$$\begin{aligned}\mu_j &= \cos\Theta\cos\Theta_j + \sin\Theta\sin\Theta_j\cos(\phi-\phi_j) \\ &= \cos\Theta\cos\Theta_j + \frac{\sin\Theta\sin\Theta_j}{2}\left[e^{i(\Theta-\Theta_j)} + e^{i(\Theta+\Theta_j)}\right] .\end{aligned} \tag{5-3.7}$$

The diagonal matrix elements involve only the first term since integrals involving $e^{\pm i\phi}$ vanish. In parabolic coordinates the diagonal matrix element $(n\ k_1 m\ |r\cos\Theta|\ n\ k_1 m)$ is given by (3-5.9):

$$(nk_1m\ |r\cos\Theta|\ nk_1m) = \frac{3}{2}\,n\,(k_1-k_2)\,a_o \ . \tag{3-5.9}$$

The phase change per collision is therefore

$$\begin{aligned}\int_{-\infty}^{\infty}(\Delta\omega_a-\Delta\omega_\alpha)dt &= \sum_{kj}\frac{2e^2}{\rho_j v_k \hbar}\cos\Theta_j\,\frac{3}{2}\,a_o\left\{[n(k_1-k_2)]_a - [n(k_1-k_2)]_\alpha\right\} \\ &= \sum_{kj}\frac{2AX_{a\alpha}}{\rho_j v_k}\cos\Theta_j \ ,\end{aligned} \tag{5-3.8}$$

where A and $X_{a\alpha}$ have their usual definitions (equation 4-1.6). The half-width $\gamma_{a\alpha}$ and frequency shift $\gamma'_{a\alpha}$ corresponding to the phase shift (5-3.8) can now be found from (3-13.12):

$$\begin{pmatrix}-\gamma_{a\alpha}\\ \gamma'_{a\alpha}\end{pmatrix} = \begin{pmatrix}R_e\\ I_m\end{pmatrix}\int_0^\infty 2\pi N v W(v)dv\int_0^\infty \rho d\rho\int_0^\Sigma \frac{d\sigma_j}{\Sigma}\left[e^{i\int_{-\infty}^{\infty}\frac{A_{a\alpha}(\sigma_j)\,dx}{(v^2x^2+\rho^2)^{n/2}}} - 1\right] . \tag{3-13.12}$$

For the interaction (5-3.3) the above expression is specialized to the case where

$$n = 3$$

$$A_{a\alpha}(\sigma_j) = AX_{a\alpha} \cos \Theta_j$$

(5-3.9)

$$v_k \to v$$

$$\int_o^{\Sigma} \frac{d\sigma_j}{\Sigma} \to \int_o^{2\pi} \frac{d\phi_j}{2\pi} \int_o^{\pi} \frac{\sin}{2} \Theta_j d\Theta_j$$

$$\gamma_{a\alpha} = 2\pi N \int_o^{\infty} vW(v)dv \int_o^{\rho_m} \rho d\rho \left(1 - \frac{\sin \frac{2AX_{a\alpha}}{\rho v}}{2AX_{a\alpha}/\rho v}\right) . \tag{5-3.10}$$

Following the discussion in Section IV.6 of the phase-shift theory as applied by Unsöld,[10] let

$$x \equiv 2 \frac{AX_{a\alpha}}{\rho v} \tag{5-3.11}$$

and

$$\tilde{\delta}_m^{a\alpha} \equiv 2 \frac{AX_{a\alpha}}{v \rho_m} = \frac{2(1.737) X_{a\alpha}}{v \rho_m} , \tag{5-3.12}$$

where ρ_m is a cutoff parameter to be discussed in Section 5 of this chapter. With the above change of variables, $\gamma_{a\alpha}$ is given by

$$\gamma_{a\alpha} = 8\pi N (AX_{a\alpha})^2 \int_o^{\infty} \frac{W(v)}{v} dv \int_{\tilde{\delta}_m^{a\alpha}}^{\infty} \frac{dx}{x^3} \left(1 - \frac{\sin x}{x}\right)$$

(5-3.13)

$$\gamma'_{a\alpha} = 0 .$$

The integral can be done by parts:

$$\int_{\delta}^{\infty} \frac{dx}{x^3} \left(1 - \frac{\sin x}{x}\right) = \frac{1}{2\delta^2} - \frac{\sin \delta}{3\delta^3} - \frac{\cos \delta}{6\delta^2} + \frac{\sin \delta}{6\delta} - \frac{1}{6} C_i(\delta) , \tag{5-3.14}$$

where $C_i(\delta)$ is the cosine integral,

$$(5\text{-}3.15)\quad C_i(\delta) = -\int_\delta^\infty \frac{\cos x}{x}\,dx = 0.5772 + \ell n\ \delta + \frac{\delta^2}{4} + \ldots$$

up to the power $(\tilde{\delta}_m^{a\alpha})^2$, $\gamma_{a\alpha}$ becomes

$$(5\text{-}3.18)\quad \gamma_{a\alpha} = 8\pi N(AX_{a\alpha})^2 \int_o^\infty \frac{W(v)}{v}\,dv\,\left[0.2094 - \frac{1}{6}\,\ell n\ \tilde{\delta}_m^{a\alpha} + \frac{(\tilde{\delta}_m^{a\alpha})^2}{240} + \ldots\right] .$$

Other authors,[10,11,15] in their consideration of electron broadening, took W(v) to be a delta function $\delta(\bar{v}-v)$, where $\bar{v}$ is the average velocity. This leads to a slight error since

$$(5\text{-}3.17)\qquad \int_o^\infty \frac{[W(v)\,dv]}{v} = \frac{\bar{1}}{v} = \frac{4}{\pi}\,\frac{1}{\bar{v}} = \frac{1.273}{\bar{v}} ,$$

where W(v) was taken to be the Boltzmann distribution for a gas in thermal equilibrium. Replacing W(v) by a delta function is seen to lead to a 27-percent discrepancy in the average half-width parameter.

Since the dependence of $\gamma_{a\alpha}$ on $\tilde{\delta}_m^{a\alpha}$ is essentially logarithmic and therefore is a slowly varying function of v, the approximation is made that

$$(5\text{-}3.18)\qquad \int_o^\infty \frac{W(v)}{v}\,dv\ \ell n\ \frac{3.47\ X_{a\alpha}}{\rho_m\ v} = \frac{\bar{1}}{v}\ \ell n\ \frac{3.47\ X_{a\alpha}}{\rho_m\ \bar{v}} .$$

In the following formulas $\tilde{\delta}_m^{a\alpha}$ is taken to be

$$(5\text{-}3.19)\qquad \tilde{\delta}_m^{a\alpha} = \frac{3.474\ X_{a\alpha}}{\rho_m \bar{v}} ,$$

so $\gamma_{a\alpha}$ is now

$$(5\text{-}3.20)\qquad \gamma_{a\alpha} = \frac{32\ N}{\bar{v}}\,(AX_{a\alpha})^2 \cdot G(\tilde{\delta}_m^{a\alpha})$$

$$G(\tilde{\delta}_m^{a\alpha}) \equiv \left(.2094 - \frac{1}{6}\,\ell n\ \tilde{\delta}_m^{a\alpha} + \frac{(\tilde{\delta}_m^{a\alpha})^2}{240} + \ldots\right) .$$

It is of interest now to compare these results with the Unsöld[10] phase-shift calculation in which all angular dependences were neglected. Taking the ratio of the Unsöld result (4-6.8) and our expression (5-3.18) for $\gamma_{a\alpha}$ yields

$$(5\text{-}3.21)\quad \frac{\gamma_{a\alpha}}{(\gamma_{a\alpha})_{\text{Unsöld}}} = \frac{16}{3\pi^3}\,\frac{(1.708 - \ell n\,\delta_m^{a\alpha} + \cdots)}{(.923 - \ell n\,\delta_m^{a\alpha})} \sim .2$$

(note that $\tilde{\delta}_m^{a\alpha} = 2\,\delta_m^{a\alpha}/\pi$).

The theory discussed by Unsöld and later applied by Griem[11] to the electron broadening of the hydrogen Balmer lines yields a result that overestimates the adiabatic contribution to the broadening by perhaps a factor of five. This agrees qualitatively with the statement by Griem* that his calculations tended to overestimate the electron broadening. Furthermore, it is seen that the present theory gives zero shift in a natural way without recourse to additional assumptions.

4. Errors in the Average Over Electron Velocities

According to the Spitzer inequality,[9] the phase-shift approximation is valid for frequencies satisfying $\Delta\omega \ll \overline{v^2}/AX_{a\alpha}$. The averaging process discussed in Chapter III included an average over the velocity v from $0 \to \infty$. This is clearly incorrect for velocities less than $\sqrt{AX_{a\alpha}\Delta\omega}$ since the phase-shift approximation fails for velocities not satisfying the Spitzer inequality.

Let us now compute the contribution to $\overline{1/v}$ from velocities less than $\sqrt{AX_{a\alpha}\Delta\omega}$ in order to estimate the errors introduced into $\gamma_{a\alpha}$ by our averaging procedure.

The Boltzmann velocity distribution is given by

*H. Griem, private communication.

$$W(v) = 4\pi \left(\frac{a}{\pi}\right)^{3/2} v^2 e^{-av^2}$$

(5-4.1)

$$a \equiv \frac{m}{2kT} ,$$

so

$$\text{(5-4.2)} \qquad \overline{\frac{1}{v}} = \int_0^\infty \frac{W(v)}{v}\, dv = 4\pi \left(\frac{a}{\pi}\right)^{3/2} \frac{1}{2a} .$$

The contribution to $\overline{1/v}$ from velocities less than $\sqrt{\Delta\omega AX_{a\alpha}}$ is given by

$$\text{(5-4.3)} \qquad \int_0^{\sqrt{\Delta\omega AX_{a\alpha}}} \frac{W(v)}{v}\, dv = 4\pi \left(\frac{a}{\pi}\right)^{3/2} \frac{\Delta\omega AX_{a\alpha}}{2} \left(1 - \frac{a\Delta\omega AX_{a\alpha}}{2} \cdots + \right) .$$

With (5-4.2) and (5-4.3) we find the percentage contribution to $\overline{1/v}$ from velocities greater than $\sqrt{\Delta\omega AX_{a\alpha}}$:

$$\text{(5-4.4)} \qquad 100\, \frac{\overline{\frac{1}{v}} - \left(\overline{\frac{1}{v}}\right)_{v < \sqrt{\Delta\omega AX_{a\alpha}}}}{\overline{\frac{1}{v}}} = 100 - 100\, \frac{a\Delta\omega AX_{a\alpha}}{2} + \cdots .$$

For temperatures of 10,000°K, a equals 3.3×10^{-16}. Consider H_β (4861Å) at 30Å from the line center. $\Delta\omega$ is of the order of 3×10^{12} and $X_{a\alpha}$ is of the order 6. For these conditions, $a\Delta\omega AX_{a\alpha} \sim 0.1$, so that 90% of the contribution to $\overline{1/v}$ comes from velocities which satisfy the Spitzer inequality. For smaller frequencies the errors introduced by treating the low-velocity end of the velocity distribution in the phase-shift approximation are correspondingly smaller. The errors increase slightly for larger $X_{a\alpha}$. However, this is not serious for H_α, H_β, and H_γ since the $X_{a\alpha}$ are of the order 1-10. A more exact theory would involve extensive numerical integrations and might be of interest with more accurate experimental data on hydrogen line broadening at high ion densities where the lines are very wide.

5. The Debye Cutoff Procedure

It was necessary to cut off our integrals over the impact parameter at some value ρ_m because of a logarithmic divergence. This difficulty is not uncommon in theories dealing with Coulomb interactions. Following Bohm and Aller[16] and Spitzer et al.,[63] the cutoff ρ_m is taken to be the collision parameter beyond which an electron is effectively screened by the neutral plasma of ions and electrons. This distance is commonly referred to as the Debye length and may be derived as follows, according to the discussion by Bohm and Aller.

The electric potential ϕ satisfies the Poisson equation

$$(5\text{-}5.1) \qquad \nabla^2\phi = -4\pi\rho = -4\pi e \left(Z_i N_i e^{-\frac{Z_i e\phi}{kT}} - N_e e^{e\phi/kT} \right) ,$$

where N_i and N_e are the particle densities of ions and electrons and $Z_i e$ is the ionic charge. On expanding the exponentials and making use of the fact that the electron density is related to the ion density by the expression $N_e = Z_i N_i$, and that for high temperatures $e\phi/kT$ is small compared to unity, the Poisson equation reduces to

$$(5\text{-}5.2) \qquad \nabla^2\phi = \frac{4\pi e^2 (Z_i+1)\,\phi}{kT} = \frac{\phi}{\rho_m^2} .$$

The solution corresponding to a point charge having a finite potential at infinity is

$$(5\text{-}5.3) \qquad \phi = \frac{e}{r} e^{-r/\rho_m} ,$$

where ρ_m is given by

$$(5\text{-}5.4) \qquad \rho_m = \left[\frac{kT}{4\pi N_e (1+Z_i) e^2} \right]^{1/2} .$$

If the ion and electron densities are equal, then $Z_i = 1$ and ρ_m is

$$\rho_m = \left(\frac{kT}{e^2 8\pi N_e}\right)^{1/2}, \tag{5-5.5}$$

and the maximum phase shift $\tilde{\delta}_m^{a\alpha}$ is given by

$$\tilde{\delta}_m^{a\alpha} = \frac{2AX_{a\alpha}}{\rho_m \bar{v}} = 1.80 \times 10^{-6} X_{a\alpha} \frac{\sqrt{N_e}}{T} . \tag{5-5.6}$$

For temperatures of the order 10,000°K and ion densities of the order $N_i \sim 10^{15}$ cm^{-3}, the Debye length ρ_m and the mean distance between ions ($\sim N_i^{-1/3}$) are very nearly equal. Therefore, on the average, an electron feels only a single ion at a time, i.e., only a single ion is contained on the average in each Debye sphere. This is a physical justification for the validity of a binary collision theory of the Foley[32] type. However, at higher temperatures, where the Debye length exceeds the mean distance between particles, the binary collision assumption necessarily fails. For this reason earlier phase-shift theories were expected to fail at high temperatures. Our theory, however, is not subject to this restriction since we have included multiple interactions in the formal theory.

6. The Effect of Close Collisions

In Section V.3 the half-width $\gamma_{a\alpha}$ was found to be

$$\gamma_{a\alpha} = \frac{32N}{\bar{v}} (AX_{a\alpha})^2 G(\tilde{\delta}_m^{a\alpha})$$

$$G(\tilde{\delta}_m^{a\alpha}) = 0.2094 - 1/6 \ln \tilde{\delta}_m^{a\alpha} + \frac{(\tilde{\delta}_m^{a\alpha})}{240} + \ldots \tag{5-3.20}$$

$$= 1/6 \, (1.2564 - \ln \tilde{\delta}_m^{a\alpha} + \ldots) .$$

The integration over the impact parameter included the range $\rho = 0 \rightarrow \rho_m$,

where ρ_m was taken to be the Debye length. The above expression for the half-width parameter $\gamma_{a\alpha}$ must be modified to take into account the close collisions. The weak collision theory developed in Chapter III fails when the matrix elements of the phase integral

$$\frac{1}{\hbar}\int_{-\infty}^{\infty} H_1(t)dt$$

are not small compared to unity. An approximate scheme for taking into account the close collisions was discussed in Section III.14 (see equations 3-14.17—3-14.20). The contribution to $\gamma_{a\alpha}$ for collisions with impact parameters small enough to give phase shifts greater than unity is given by the kinetic-theory result

$$(5\text{-}6.1)\qquad (\gamma_{a\alpha})_{\rho<\rho_c} = \frac{1}{\tau_c} = \pi\,\rho_c^2\,N\bar{v} = \text{mean time between collisions}\ ,$$

where ρ_c is determined by the condition that the phase shift per collision is unity

$$(5\text{-}6.2)\qquad \tilde{\delta}_c^{a\alpha} = 1 = \frac{2AX_{a\alpha}}{\rho_c\,\bar{v}}\ ,$$

so

$$(5\text{-}6.3)\qquad \rho_c = \frac{2AX_{a\alpha}}{\bar{v}}\ .$$

Hence

$$(5\text{-}6.4)\qquad (\gamma_{a\alpha})_{\rho<\rho_c} = \frac{4\pi}{\bar{v}}\,(AX_{a\alpha})^2\,N\ .$$

The contribution to $\gamma_{a\alpha}$ from the weak collisions is found by integrating over the impact parameter from $\rho_c \to \rho_m$ instead of from $0 \to \rho_m$.

$$(5\text{-}6.5)\qquad (\gamma_{a\alpha})_{\rho>\rho_c} = \frac{32N}{\bar{v}}\,(AX_{a\alpha})^2\,[G(\tilde{\delta}_m^{a\alpha}) - G(1)]\ .$$

According to the expression (5-3.20), G(1) is given by

$$G(1) = .2094 + \frac{1}{240} = .2136 \quad , \tag{5-6.6}$$

so

$$(\gamma_{a\alpha})_{\rho > \rho_c} = \frac{32N}{\bar{v}} (AX_{a\alpha})^2 \left(-1/6 \ln \tilde{\delta}_m^{a\alpha} - .0042\right)$$

$$\cong - \frac{16N}{3\bar{v}} (AX_{a\alpha})^2 \ln \tilde{\delta}_m^{a\alpha} \quad . \tag{5-6.7}$$

The total width, taking into account both strong and weak collisions, is found by adding (5-6.5) and (5-6.7):

$$\gamma_{a\alpha} = \frac{16N}{3\bar{v}} (AX_{a\alpha})^2 (2.36 - \ln \tilde{\delta}_m^{a\alpha} + \ldots) \quad . \tag{5-6.8}$$

In the pure weak collision theory (where the integration over the impact parameter is carried out from $\rho = 0 \to \infty$) the half-width parameter was found to be

$$(\gamma_{a\alpha})_{weak} = \frac{16N}{3\bar{v}} (1.26 - \ln \tilde{\delta}_m^{a\alpha} + \ldots) \quad . \tag{5-3.20}$$

The difference between the two results is negligible if

$$(2.36 - 1.26) = 1.10 \ll \ln \frac{1}{\tilde{\delta}_m^{a\alpha}} \quad . \tag{5-6.9}$$

When this criterion is satisfied, the distant collisions are mainly responsible for the broadening. For example, when $N_e = 10^{15}$, $T = 20{,}000^\circ K$, and $X_{a\alpha} = 1.10$, then

$$\ln \frac{1}{\tilde{\delta}_m^{a\alpha}}$$

ranges from 5.86 to 3.56. The rather <u>ad hoc</u> procedure for treating the close collisions introduces an uncertainty of perhaps 10-20 percent into

the expression 5-3.20 for the half-width parameter $\gamma_{a\alpha}$.

7. The Broadening of Lyman α by Electrons

The broadening of the Lyman α line due to electron collisions will now be considered in detail. The line originates from a transition between a fourfold degenerate state (n=2) and the ground state (n=1) of hydrogen. The passing electrons cause both transitions among the degenerate substates (nonadiabatic effect) and phase shifts (adiabatic effect). It will be shown that the adiabatic and nonadiabatic contributions to the broadening are comparable. The quantitative results will be compared with other theories.

7a. Wavefunctions and Matrix Elements

It will be convenient first to calculate the matrix elements of interest in the Lyman α problem. The wavefunctions $\phi_{n,\ell,m}$ corresponding to the states with principal quantum numbers n=2 and 1 are

$$\phi_{2,1,\pm1} = \frac{r}{8\sqrt{\pi}\, a_o^{5/2}}\, e^{-r/2a_o}\, e^{\pm i\phi} \sin\theta$$

$$\phi_{2,1,0} = \frac{r}{4\sqrt{2\pi}\, a_o^{5/2}}\, e^{-r/2a_o} \cos\theta$$

(5-7a.1)

$$\phi_{2,0,0} = \frac{1}{4\sqrt{2\pi}} \frac{(2-r)}{a_o}\, e^{-r/2a_o}$$

$$\phi_{1,0,0} = \frac{1}{\sqrt{\pi}} \frac{1}{a_o^{3/2}}\, e^{-r/a_o} \quad .$$

The appropriate stabilized eigenfunctions for a hydrogen atom in an external static electric field are given by

$$\phi_+ = \frac{1}{\sqrt{2}} (\phi_{2,0,0} + \phi_{2,1,0})$$

(5-7a.2)
$$\phi_- = \frac{1}{\sqrt{2}} (\phi_{2,0,0} - \phi_{2,1,0})$$

$$\phi_{2,1,\pm 1} \quad .$$

If the ion broadening is neglected so that there is no associated static electric field, then the electron broadening can be calculated with either set of wavefunctions. If, however, in addition to the rapidly fluctuating electronic electric field there is a static ion field, then one must employ the set of functions (5-7a.2) since these wavefunctions describe the perturbed hydrogen atom between electron collisions. This point will be discussed at length later when both ion and electron perturbations will be considered simultaneously.

For the electron broadening one is interested in matrix elements of the phase integral

$$\int_{-\infty}^{\infty} H_j(\tau) d\tau$$

which, according to (5-3.6) and (5-3.7), involve the matrix elements of

(5-7a.3) $$r\,\mu_j = r\left\{\cos\Theta\cos\Theta_j + \frac{\sin\Theta\sin\Theta_j}{2}\left[e^{i(\phi-\phi_j)} + e^{-i(\phi-\phi_j)}\right]\right\} .$$

The radial integrals involved in the computation of the various matrix elements are trivial and can all be done easily by a series of partial integrations. The result of the calculations is as follows:

$$\langle 2,1,\pm 1 | r\mu_j | 2,1,\pm 1\rangle = 0$$

$$\langle 2,1,0 | r\mu_j | 2,1,0\rangle = 0$$

$$\langle 2,0,0 \mid r\mu_j \mid 2,0,0\rangle = 0$$

$$\langle 2,1,0 \mid r\mu_j \mid 2,0,0\rangle = 3a_o \cos\theta_j$$

$$\langle 2,0,0 \mid r\mu_j \mid 2,1,+1\rangle = \frac{3a_o}{\sqrt{2}} \sin\theta_j \, e^{+i\phi_j}$$

$$\langle 2,0,0 \mid r\mu_j \mid 2,1,-1\rangle = \frac{3a_o}{\sqrt{2}} \sin\theta_j \, e^{-i\phi_j}$$

$$\langle 2,1,0 \mid r\mu_j \mid 2,1,\pm 1\rangle = 0$$

$$\langle + \mid r\mu_j \mid + \rangle = 3a_o \cos\theta_j$$

$$\langle - \mid r\mu_j \mid - \rangle = -3a_o \cos\theta_j$$

$$\langle + \mid r\mu_j \mid 2,1,\pm 1\rangle = \frac{3}{2} a_o \sin\theta_j \, e^{\pm i\phi_j}$$

(5-7a.4)

$$\langle - \mid r\mu_j \mid 2,1,\pm 1\rangle = \frac{3}{2} a_o \sin\theta_j \, e^{\pm i\phi_j}$$

$$\langle + \mid r\mu_j \mid - \rangle = 0 \quad ,$$

where a_o is again the first Bohr radius. The intensity of the observed radiation also depends on the dipole matrix elements which are tabulated below:

$$\langle 2,1,+1 \mid x \mid 1,0,0\rangle = -i \frac{R_{21}}{6a_o^4}$$

$$\langle 2,1,-1 \mid x \mid 1,0,0\rangle = +i \frac{R_{21}}{6a_o^4}$$

$$\langle 2,1,\pm 1 \mid y \mid 1,0,0\rangle = \frac{R_{21}}{6a_o^4} \qquad R_{21} \equiv \int_o^\infty r^4 \, e^{-3r/2a_o} \, dr$$

$$\langle 2,1,0 \mid z \mid 1,0,0\rangle = \frac{\sqrt{2} R_{21}}{6a_o^4}$$

(5-7a.5)

$$\langle 2,0,0 \mid x,y,z \mid 1,0,0\rangle = 0$$

$$\langle 2,1,0 \mid x,y \mid 1,0,0\rangle = 0$$

$$\langle 2,1,\pm 1 \mid z \mid 1,0,0\rangle = 0$$

$$< + \quad |z|1,0,0> = \frac{R_{21}}{6a_o^4}$$

$$< - \quad |z|1,0,0> = -\frac{R_{21}}{6a_o^4}$$

$$< + \quad |x,y|1,0,0> = 0$$

$$< - \quad |x,y|1,0,0> = 0$$

7b. The Broadening of the Lyman α Line Using the Wavefunctions (5-7a.1)

Let us now compute the broadening of the Lyman α line using the hydrogen wavefunctions (5-7a.1). Since we are neglecting the ion broadening here, $\omega^o_{\alpha\beta} = 0$ and the expression for $I_{a\alpha}(\omega)$ reduces to

$$I_{a\alpha}(\omega) = \frac{\Gamma_{a\alpha}}{\pi(\Delta\omega^o_{a\alpha})^2} \quad , \tag{5-7b.1}$$

where $\Gamma_{a\alpha}$ is defined by

$$\Gamma_{a\alpha} = \Gamma_{(1,0,0)\alpha} = \frac{1}{2\hbar^2} \sum_j \left| \int_{-\infty}^{\infty} d\tau \sum_\beta \mu^o_{(1,0,0)\beta} [H_j(\tau)]_{\beta\alpha} \right|^2_{\text{Avg}} \tag{5-7b.2}$$

$$\alpha = (2,0,0),\ (2,1,0),\ (2,1,+1),\ (2,1,-1) \quad .$$

With the table of matrix elements (5-7a.4) and (5-7a.5) it is readily verified that only $\Gamma_{(1,0,0)(2,0,0)}$ is nonzero:

$$\Gamma_{(1,0,0)(2,0,0)} = \frac{1}{2\hbar^2} \sum_j \left| \int_{-\infty}^{\infty} d\tau \left\{ \mu^o_{(1,0,0)(2,0,0)} [H_j(\tau)]_{(2,0,0)(2,0,0)} \right.\right. \tag{5-7b.3}$$

$$+ \mu^o_{(1,0,0)(2,1,0)} [H_j(\tau)]_{(2,1,0)(2,0,0)} + \mu^o_{(1,0,0)(2,1,1)} \cdot$$

$$\left.\left. \cdot [H_j(\tau)]_{(2,1,1)(2,0,0)} + \mu^o_{(1,0,0)(2,1,-1)} [H_j(\tau)]_{(2,1,-1)(2,0,0)} \right\} \right|^2_{\text{Avg}} .$$

According to (5-3.4), the phase integral is given by

$$(5\text{-}3.4) \qquad \int_{-\infty}^{\infty} H_j(\tau)d\tau = \frac{2e^2}{v\,\rho_j}\, r\mu_j \ ,$$

where $r\mu_j$ is given by (5-7a.3). Since $\langle 2,0,0|r\mu_j|2,0,0\rangle=0$, $\Gamma_{(1,0,0)(2,0,0)}$ is now

$$\Gamma_{(1,0,0)(2,0,0)} \sum_j \left\{ \frac{2e^4}{v^2\rho_j^2\hbar^2} \left| \mu^o_{(1,0,0)(2,1,0)}[r\mu_j]_{(2,1,0)(2,0,0)} \right.\right.$$

$$+ \mu^o_{(1,0,0)(2,1,1)}[r\mu_j]_{(2,1,1)(2,0,0)}$$

$$\left.\left. + \mu^o_{(1,0,0)(2,1,-1)}[r\mu_j]_{(2,1,-1)(2,0,0)} \right|^2 \right\}_{\text{Avg}} ,$$

where we have abbreviated the matrix elements $\langle \alpha|r\mu_j|\beta\rangle$ by $[r\mu_j]_{\alpha\beta}$. Now $\mu^o_{(1,0,0)(2,1,\pm1)}$ receives contributions from the x and y matrix elements corresponding to radiation with different polarizations and can be written

$$\mu^o_{(1,0,0)(2,1,\pm1)} = [y]_{(1,0,0)(2,1,1)}\, e^{i\eta} \mp [x]_{(1,0,0)(2,1,1)}$$

$$(5\text{-}7b.5) \qquad [x]_{(1,0,0)(2,1,1)} = -[x]_{(1,0,0)(2,1,-1)}$$

$$[y]_{(1,0,0)(2,1,1)} = +[y]_{(1,0,0)(2,1,-1)}$$

$$(5\text{-}7b.6) \qquad \left|[x]_{(2,1,1)(1,0,0)}\right| = \left|[y]_{(2,1,1)(1,0,0)}\right| \ .$$

On averaging over the random phase η between the y and x radiation one finds

$$(5\text{-}7b.7) \qquad \left|\mu^o_{(1,0,0)(2,1,\pm1)}\right|^2 = 2\left|[x]_{(1,0,0)(2,1,\pm1)}\right|^2 \ .$$

On substituting for the various matrix elements into (5-7b.4), using the

above relations with (5-7a.4) and (5-7a.5), the following result is obtained:

$$\Gamma_{(1,0,0)(2,0,0)} = \sum_j \left\{ \frac{2e^4}{v^2 \rho_j^2 \hbar^2} \left| \sqrt{2} \cdot \frac{R_{21}}{6a_0^4} \cdot 3a_0 \cos\theta_j \right.\right.$$

(5-7b.8)

$$\left.\left. + \frac{R_{21}}{6a_0^4} \left[(e^{i\eta}+1)e^{-i\phi_j} \frac{3a_0}{\sqrt{2}} \sin\theta_j + (e^{i\eta}-1) \frac{3a_0}{\sqrt{2}} \sin\theta_j \, e^{+i\phi_j} \right] \right|^2 \right\}_{Avg} .$$

On squaring and averaging, all terms involving exp $i\eta$ and (sin θ_j cos θ_j) vanish. Hence

$$\Gamma_{(1,0,0)(2,0,0)} = \sum_j \left[\left(\frac{6e^2 a_0}{v\rho_j \hbar} \right)^2 \left(\frac{R_{21}}{6a_0^4} \right)^2 (\cos^2\theta_j \right.$$

(5-7b.9)

$$\left. + \sin^2\theta_j \, |\cos\theta_j \, e^{i\eta} + \sin\theta_j|^2) \right]_{Avg}$$

$$\Gamma_{(1,0,0)(2,0,0)} = \sum_j \left[\left(\frac{6e^2 a_0}{v\rho_j \hbar} \right)^2 \left(\frac{R_{21}}{6a_0^4} \right)^2 (\cos^2\theta_j + \sin^2\theta_j) \right]_{Avg}$$

(5-7b.10)

$$= \left| \mu^0_{+(1,0,0)} \right|^2 \sum_j \left(\frac{6e^2 a_0}{v\rho_j \hbar} \right)^2_{Avg} .$$

This broadening arises solely from nonadiabatic transitions since the diagonal matrix elements all vanish with the $\phi_{2,0,0}$ $\phi_{2,0,\pm1}$ $\phi_{2,1,0}$ set of wavefunctions. Let us now compare these results with a calculation using the Stark wavefunctions (5-7a.2).

7c. The Broadening of the Lyman α Line Using the Wavefunctions (5-7a.2)

The broadening of the Lyman α line of hydrogen will be computed again with the set of wavefunctions (5-7a.2)(i.e., the set ϕ_+, ϕ_-, $\phi_{2,1,\pm1}$). The final result is identical to the result obtained with the set of wavefunctions (5-7a.1) and is included in order to illustrate the importance of

nonadiabatic transitions in the theory and to facilitate the comparison with other theories of hydrogen line broadening. It is also to be remembered that one must use the Stark wavefunctions when a static ion field is present.

It is readily verified that $\Gamma_{(1,0,0)_+} = \Gamma_{(1,0,0)_-}$ for the displaced Stark components. Since the calculations are similar to those of the previous section, the details will not be given. In addition, the term $\Gamma_{(1,0,0)(2,1,\pm1)}$ is again zero (previous section).

Let us consider now the terms $\Gamma_{(1,0,0)_+} = \Gamma_{(1,0,0)_-}$:

$$\Gamma_{(1,0,0)_+} = \sum_j 2\left\{\left(\frac{e^2}{v\rho_j\hbar}\right)^2 \left| \mu^o_{(1,0,0)_+}\,[r\mu_j]_{++} + \mu^o_{(1,0,0)(2,1,1)}[r\mu_j]_{(2,1,1)_+}\right.\right.$$

(5-7c.1)

$$\left.\left. + \mu^o_{(1,0,0)(2,1,-1)}[r\mu_j]_{(2,1,-1)_+}\right|^2\right\}_{Avg} .$$

Now according to (5-7a.4) and (5-7a.5),

$$\mu^o_{(1,0,0)_+} = \frac{\mu_{(1,0,0)(2,1,0)}}{\sqrt{2}}$$

(5-7c.2)
$$[r\mu_j]_{(2,1,1)_+} = \frac{[r\mu_j]}{\sqrt{2}}\,(2,1,1)(2,0,0)$$

$$[r\mu_j]_{++} = [r\mu_j]_{(2,1,0)(2,0,0)} .$$

With these substitutions, $\Gamma_{(1,0,0)_+}$ becomes

$$\Gamma_{(1,0,0)_+} = \frac{1}{2}\sum_j \left\{\frac{2e^4}{v^2\rho_j^2\hbar^2}\left| \mu^o_{(1,0,0)(2,1,0)}[r\mu_j]_{(2,1,0)(2,0,0)}\right.\right.$$

(5-7c.3)
$$+ \mu^o_{(1,0,0)(2,1,1)}\,[r\mu_j]_{(2,1,1)(2,0,0)}$$

$$\left.\left. + \mu_{(1,0,0)(2,1,-1)}\,[r\mu_j]_{(2,1,-1)(2,0,0)}\right|^2\right\}_{Avg} .$$

Comparing this expression with (5-7b.4), one finds that

$$\Gamma_{(1,0,0)_+} = \frac{1}{2}\Gamma_{(1,0,0)(2,0,0)} \quad . \tag{5-7c.4}$$

The broadening arises from both $\Gamma_{(1,0,0)_+}$ and $\Gamma_{(1,0,0)_-}$ so that

$$I(\omega) = \frac{\Gamma_{(1,0,0)_+} + \Gamma_{(1,0,0)_-}}{\pi(\Delta\omega)^2} = \frac{\Gamma_{(1,0,0)(2,0,0)}}{\pi(\Delta\omega)^2} \quad . \tag{5-7c.5}$$

Therefore, it is verified that either set of wavefunctions leads to the same result. There is, however, an interesting comparison between the two calculations. With the set of wavefunctions (5-7a.1), all the broadening arises from nonadiabatic effects. However, the broadening is partly due to nonadiabatic effects and partly due to adiabatic effects with the Stark wavefunctions (5-7a.2). The ratio of the adiabatic to nonadiabatic broadening in the second case is found from the ratio of the two terms in (5-7b.10):

$$\frac{\Gamma_{\text{adiabatic}}}{\Gamma_{\text{nonadiabatic}}} = \frac{\langle\cos^2\theta_j\rangle_{\text{Avg}}}{\langle\sin^2\theta_j\rangle_{\text{Avg}}} = \frac{1}{2} \quad , \tag{5-7c.6}$$

so that

$$\Gamma_{(1,0,0)(2,0,0)} = \Gamma_{(1,0,0)_+} + \Gamma_{(1,0,0)_-} = \Gamma_{\text{adiabatic}} + 2\Gamma_{\text{adiabatic}} \tag{5-7c.7}$$

and the absorption coefficient is accordingly

$$I(\omega) = \frac{3\Gamma_{\text{Ad}}}{\pi\Delta\omega^2} \quad . \tag{5-7c.8}$$

From this example it can be seen that it is necessary to include both nonadiabatic and adiabatic effects in the theory of hydrogen line broadening by electron collisions.

If one requires that the absorption coefficient (5-7c.8) be normalized to $2|\mu^{o}_{+(1,0,0)}|^2$ (i.e., the line strength of the displaced Stark components), then one can determine the appropriate damping constant. This procedure leads to the following result:

$$I(\omega) = \frac{2|\mu^{o}_{+(1,0,0)}|^2}{\pi} \cdot \frac{\gamma}{\Delta\omega^2 + \gamma^2} \tag{5-7c.9}$$

where

$$\gamma = \frac{3\Gamma_{Ad}}{2|\mu^{o}_{+(1,0,0)}|^2} = 18\left(\frac{a_o e^2}{\hbar}\right)^2 \sum_j \left(\frac{1}{v^2\rho_j^2}\right)_{Avg} . \tag{5-7c.10}$$

Now there are $2\pi\rho_j d\rho_j Nv$ collisions per second with impact parameter between $(\rho_j, \rho_j+d\rho_j)$ so that γ is given by

$$\gamma = \frac{18a_o^2 e^4}{\hbar^2} \cdot 2\pi N \int_{\rho_c}^{\rho_m} d\rho_j \, \rho_j \left(\frac{1}{\rho_j^2 v}\right)_{\text{Avg over v}} \tag{5-7c.11a}$$

$$\gamma = \frac{36\pi a_o^2 e^4}{\hbar^2} N \overline{\frac{1}{v}} \ln\frac{\rho_m}{\rho_c} . \tag{5-7c.11b}$$

But

$$\overline{\frac{1}{v}} = \frac{4}{\pi}\frac{1}{\bar{v}}$$

so that γ is finally given by

$$\gamma = \frac{144\, a_o^2 e^4}{\hbar^2} \frac{N}{\bar{v}} \ln\frac{\rho_m}{\rho_c} \tag{5-7c.12}$$

and

$$\gamma_{Ad} = \frac{\gamma}{3} = \frac{48\, a_o^2 e^4}{\hbar^2} \frac{N}{\bar{v}} \ln\frac{\rho_m}{\rho_c} . \tag{5-7c.13}$$

This result is to be compared with the result of the adiabatic theory (5-6.7):

$$(5\text{-}6.7) \qquad \gamma_{a\alpha} = \gamma_{(1,0,0)+} = \frac{16N}{3\bar{v}} [AX_{(1,0,0)+}] \ln \frac{\rho_m}{\rho_c} \ .$$

For Lyman α, $X_{a\alpha} = 2$ so that with the definition of A (3-1.6)

$$(5\text{-}7c.14) \qquad AX_{(1,0,0)_+} = \left(\frac{3}{2} e^2 a_0\right) \cdot 2$$

and

$$(5\text{-}7c.15) \qquad \gamma_{(1,0,0)+} = \frac{48\, a_0^2\, e^4}{\hbar^2} \frac{N}{\bar{v}} \ln \frac{\rho_m}{\rho_c} \ ,$$

which agrees with (5-7c.13) as it should.

8. Comparison of the Classical Path Theory with a Recent Quantum Mechanical Calculation

In a recent paper by Kivel, Bloom, and Margenau[15] a theory of the electron broadening of the Lyman α line was presented. This theory was completely quantum mechanical. The electrons were described by plane waves (Born approximation) and the states of the hydrogen atom were taken to be the set of Stark wavefunctions (5-7a.2). It has been verified that the perturbation matrix elements computed according to the classical path theory and those computed quantum mechanically are identical. The reason for this is that the distant collisions are mainly responsible for the broadening so that the plane-wave approximation for the electron wavefunction is quite good. The classical path approximation is also valid because of the large orbital angular momentum associated with the distant collisions.

In order to show the equivalence of the classical path and quantum theories, it was necessary to compute the diagonal perturbation matrix element with the wavefunction Φ_+ in the quantum mechanical theory. This matrix element (which was not computed by Kivel, Bloom, and Margenau) is

large and contributes one-third of the broadening using the Stark wavefunctions. This is equivalent to the adiabatic part of the broadening in the classical path theory. In the Kivel, Bloom, and Margenau (KBM) theory this is referred to as the "universal" broadening. The broadening computed in KBM was due mainly to the $(+) \rightarrow (2,1,\pm1)$; $(-) \rightarrow (2,1,\pm1)$ transitions induced by the passing electrons. This was called the "polarization by induction" broadening and is the "nonadiabatic" effect referred to in our classical path theory. A third source of broadening due to $(+) \rightarrow (-)$ transitions was found to be small in the quantum theory and zero in the classical path theory. This broadening was called "polarization by reorientation" by KBM.

The only other differences between KBM and our treatment are: (1) in the choice of the critical impact parameters with which one cuts off the divergent integrals that appear in the theory (because of the logarithmic nature of the divergence this difference is small, about 20 percent); (2) our treatment includes a velocity averaging; and (3) the KBM theory did not include a discussion of how to weight the various perturbation matrix elements with the dipole matrix elements $\mu^{o}_{a\alpha}$. Including the diagonal matrix element $[H_1]_{+,+}$ together with $[H_1]_{+,(2,1,\pm1)}$ in the quantum theory and weighting these elements with $\mu_{+,(1,0,0)}$ and $\mu_{(2,1,\pm1)(1,0,0)}$ yields a half-width γ that is three times that given in KBM. In comparing the electron broadening with the usual Holtsmark ion broadening it is also to be remembered that there are two displaced Stark components. The wing intensity due to electron broadening is given by

$$I(\omega) = \frac{2}{\pi} \left| \mu^{o}_{+(1,0,0)} \right|^2 \frac{\gamma}{\Delta\omega^2+\gamma^2} = \frac{1}{\pi} \left| \mu^{o}_{+(1,0,0)} \right|^2 \frac{6\gamma_{KBM}}{\Delta\omega^2+(3\gamma_{KBM})^2} \, .$$

Accordingly, the ratio of the electron broadening to the ion broadening is some six times that given in KBM. A more detailed comparison between the electron broadening and ion broadening will be made in subsequent sections of this chapter.

9. Comparison with the Inglis-Teller Theory

In the Inglis-Teller[12] theory of electron broadening discussed in Section IV.5 it was found that the broadening of the ϕ_+ state was proportional to the following matrix element:

$$\left[\int_{-\infty}^{\infty} H_j^2(\tau)\, d\tau\right]_{++}$$

If one employs the phase integral given by (5-3.4) and computes the above matrix element exactly with the wavefunction

$$\Phi_+ = \frac{1}{\sqrt{2}}\left(\Phi_{2,0,0} + \Phi_{2,1,0}\right)$$

instead of using the Inglis-Teller estimate, then the result for Lyman α is in complete agreement with our calculations and also with the quantum theory of Kivel, Bloom, and Margenau.[15]

The agreement between our classical path theory and considerations of the Inglis-Teller type is not expected necessarily to give identical results for the other Balmer lines. The reason for this is that the matrix element

$$\int_{-\infty}^{\infty} [H_j^2(t)]_{\alpha\alpha}\, dt$$

contains all the nondiagonal matrix elements $[H_j(t)]_{\alpha a}$, including those between states of different principal quantum numbers. Our theory considers transitions only among the degenerate substates of hydrogen and neglects transitions between states of different principal quantum number.

The classical path theory cannot be used to treat transitions between states whose energy difference is not small compared to the mean kinetic energy of the perturbers.

10. Hydrogen Line Broadening by Both Ions and Electrons

In a partially ionized gas the spectral lines of hydrogen are broadened by collisions with both ions and electrons. In our "weak collision" theory for the broadening due to high-velocity electrons, a static field splitting of the normally degenerate hydrogen states was introduced. This splitting is presumed to be due to the Stark effect of the static ion field.

In this section both ions and electrons will first be taken into account in the adiabatic approximation to the theory. This can be done exactly for slow ions and fast electrons where the statistical and phase-shift approximations are valid. The results can then be generalized to include nonadiabatic effects for frequencies large compared to the half-width for electron broadening. For frequencies smaller than the half-width due to electron broadening the divergence of our basic equations does not allow us to obtain explicit formulas for the line core ($\Delta\omega < \gamma_{a\alpha}$) in the nonadiabatic case.

10a. Ion and Electron Broadening in the Adiabatic Approximation

According to the adiabatic approximation to the classical path theory, the absorption coefficient is given by

$$(3\text{-}10.7)\quad I_{a\alpha}(\omega) = \frac{|\mu^{o}_{a\alpha}|^2}{\pi} R_e \int_0^\infty d\tau\, e^{-i\Delta\omega^{o}_{a\alpha}\tau} \left[e^{i\int_0^\tau (\Delta\omega_a - \Delta\omega_\alpha)dt} \right]_{Avg} .$$

If the perturbing particles are ions and electrons, the phase integral is given by

$$(5\text{-}10a.1)\quad \int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)dt = \int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)_{ions}\, dt + \int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)_{electrons}\, dt \,.$$

In the statistical approximation the perturbation due to the ions is time independent:

$$(4\text{-}1.5)\quad \int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)_{ions}\, dt = \frac{AX_{a\alpha}}{e} F\tau$$

where e is the charge of the ion and F is the instantaneous ion field strength at the radiating atom. The absorption coefficient is now

$$(5\text{-}10a.2)\quad I_{a\alpha}(\omega) = \frac{|\mu^o_{a\alpha}|^2}{\pi} R_e \int_o^\infty d\tau \left[e^{\left(-i\Delta\omega^o_{a\alpha} + i \frac{AX_{a\alpha}}{e} F\right)\tau + i\int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)_{electrons} dt} \right]_{Avg} .$$

If all correlations between the electron and ion positions are neglected in the statistical averaging, then the results of Section V.3 can be used directly for the average over the electron coordinates

$$(5\text{-}10a.3)\quad \left[e^{\, i\int_o^\tau (\Delta\omega_a - \Delta\omega_\alpha)_{electrons}\, dt} \right]_{Avg} = e^{-\gamma_{a\alpha}\tau}$$

and the absorption coefficient becomes

$$(5\text{-}10a.4)\quad I_{a\alpha}(\omega) = \frac{|\mu^o_{a\alpha}|^2}{\pi} R_e \left[\int_o^\infty e^{-i\left(\Delta\omega^o_{a\alpha} - \frac{AX_{a\alpha}}{e} F\right)\tau - \gamma_{a\alpha}\tau} d\tau \right]_{Avg(ions)} .$$

The integration over τ yields

$$I_{a\alpha}(\omega) = \frac{|\mu^o_{a\alpha}|^2}{\pi} \left[\frac{\gamma_{a\alpha}}{\left(\Delta\omega^o_{a\alpha} - AX_{a\alpha}\frac{F}{e}\right)^2 + \gamma^2_{a\alpha}} \right]_{Avg(ions)}$$

$$(5\text{-}10a.5)\quad = \frac{|\mu^o_{a\alpha}|^2}{\pi} \gamma_{a\alpha} \int_o^\infty W(\Lambda)d\Lambda \frac{1}{(\Delta\omega^o_{a\alpha} - AX_{a\alpha}\Lambda)^2 + \gamma^2_{a\alpha}} \,,$$

where $W(\Lambda)d\Lambda$ is the probability distribution of the quantity F/e. According to (4-1.10) and (4-1.21), $W(\Lambda)d\Lambda$ is given by the Holtsmark distribution

$$(4\text{-}1.21)\quad W(|\vec{\Lambda}|)\,d|\vec{\Lambda}| \equiv W(\Lambda)d\Lambda = \frac{2}{\pi}\Lambda d\Lambda \int_0^\infty \xi d\xi \sin \Lambda\ \xi\ e^{-4.21\ N_i \xi^{3/2}},$$

where N_i is the ion density.

With the above expression for $W(\Lambda)$, the absorption coefficient is now

$$(5\text{-}10a.6)\quad I_{a\alpha}(\omega) = \frac{2}{\pi^2}\,|\mu^o_{a\alpha}|^2\,\gamma_{a\alpha}\int_0^\infty \xi d\xi\ e^{-4.21N_i\xi^{3/2}} \int_0^\infty \frac{(\sin \Lambda\ \xi)\ \Lambda d\Lambda}{(\Delta\omega_{a\alpha}-AX_{a\alpha}\Lambda)^2+\gamma_{a\alpha}{}^2}.$$

Since the broadening is symmetrical about the line center, the integral over Λ must include both the high- and low-frequency Stark components. The absorption coefficient for all frequencies is then

$$I_{a\alpha}(\omega) = \frac{2}{\pi^2}\,|\mu^o_{a\alpha}|^2\,\gamma_{a\alpha}\int_0^\infty \xi d\xi\ e^{-4.21N_i\xi^{3/2}}\cdot$$

$$(5\text{-}10a.7)\qquad \cdot\int_0^\infty \Lambda \sin \Lambda\ \xi\ d\Lambda \left[\frac{1}{(\Delta\omega^o_{a\alpha}+AX_{a\alpha}\Lambda)^2+\gamma^2} + \frac{1}{(\Delta\omega^o_{a\alpha}-AX_{a\alpha}\Lambda)^2+\gamma^2_{a\alpha}}\right],$$

but

$$(5\text{-}10a.8)\qquad \int_0^\infty \frac{\Lambda \sin \Lambda\ \xi\ d\Lambda}{(\Delta\omega^o_{a\alpha}+AX_{a\alpha}\Lambda)^2+\gamma^2_{a\alpha}} = \int_{-\infty}^0 \frac{\Lambda \sin \Lambda\ \xi\ d\Lambda}{(\Delta\omega^o_{a\alpha}-AX_{a\alpha}\Lambda)^2+\gamma^2_{a\alpha}}$$

so that (5-10a.7) becomes

$$(5\text{-}10a.9)\quad I_{a\alpha}(\omega) = \frac{2}{\pi^2}\,|\mu^o_{a\alpha}|^2\,\gamma_{a\alpha}\int_0^\infty \xi d\xi\ e^{-4.21N_i\xi^{3/2}} \int_{-\infty}^\infty \frac{\Lambda \sin \Lambda\ \xi\ d\Lambda}{(\Delta\omega^o_{a\alpha}-AX_{a\alpha}\Lambda)^2+\gamma_{a\alpha}{}^2}.$$

The integral over Λ can be done simply by a coutour integration

$$(5\text{-}10a.10)\int_{-\infty}^\infty \frac{\Lambda \sin \Lambda\ \xi\ d\Lambda}{(\Delta\omega^o_{a\alpha}-AX_{a\alpha}\Lambda)^2+\gamma_{a\alpha}{}^2} = \frac{\pi\, e^{-\frac{\gamma_{a\alpha}\ \xi}{AX_{a\alpha}}}}{(AX_{a\alpha})^2\gamma_{a\alpha}}\left(\Delta\omega^o_{a\alpha}\sin\frac{\Delta\omega^o_{a\alpha}\xi}{AX_{a\alpha}} + \gamma_{a\alpha}\cos\frac{\Delta\omega^o_{a\alpha}\xi}{AX_{a\alpha}}\right).$$

The absorption coefficient is therefore

$$I_{a\alpha}(\omega) = \frac{2}{\pi} \frac{|\mu^{o}_{a\alpha}|^2}{(AX_{a\alpha})^2} \int_0^\infty \xi d\xi \, e^{(-4.21\, AX_{a\alpha} N_i \xi^{3/2} - \gamma_{a\alpha}\xi)} \frac{1}{AX_{a\alpha}} \quad .$$

(5-10a.11)

$$\cdot \left(\Delta\omega^{o}_{a\alpha} \sin \frac{\Delta\omega^{o}_{a\alpha}\xi}{AX_{a\alpha}} + \gamma_{a\alpha} \cos \frac{\Delta\omega^{o}_{a\alpha}\xi}{AX_{a\alpha}} \right) \quad .$$

It is immediately verified that this reduces to the Holtsmark distribution (4-1.24) in the limit of zero electron density ($\gamma_{a\alpha} \to 0$) and to the dispersion line shape for zero ion density.

10b. A Series Expansion for Small Frequencies

For a given spectral line one may calculate the electron half-width parameter $\gamma_{a\alpha}$ according to the weak collision theory and then evaluate numerically the expression (5-10a.11) for the absorption coefficient $I_{a\alpha}(\omega)$. Although the integral in (5-10a.11) is not expressible in closed form, it is convenient to derive asymptotic limits of the integral for large and small frequencies $\Delta\omega^{o}_{a\alpha}$ to facilitate the numerical calculations.

Consider now the integral

$$(5\text{-}10b.11) \qquad \int_0^\infty \xi d\xi \begin{matrix} \sin \\ \cos \end{matrix} \frac{\Delta\omega^{o}_{a\alpha}\xi}{AX_{a\alpha}} \, e^{(-4.21\, N_i AX_{a\alpha} \xi^{3/2} - \gamma_{a\alpha}\xi)} \frac{1}{AX_{a\alpha}} \quad .$$

Now let $\xi = AX_{a\alpha}x$, then this integral becomes

$$(5\text{-}10b.2) \qquad (AX_{a\alpha})^2 \int_0^\infty x dx \begin{matrix} \sin \\ \cos \end{matrix} \Delta\omega^{o}_{a\alpha} x \, e^{-(\lambda_{a\alpha}x)^{3/2} - \gamma_{a\alpha}x} \quad ,$$

where $\lambda_{a\alpha}$ is the ion half-width parameter defined earlier in our discussion of the Holtsmark theory,

$$(4\text{-}1.23) \qquad \lambda_{a\alpha} \equiv 4.52\, X_{a\alpha} N_i^{2/3} \quad .$$

The expression $\lambda_{a\alpha}$ is simply the Stark shift in units of circular frequency

that corresponds to the familiar Holtsmark mean field strength. With the above change of variables, the absorption coefficient is given by

$$I_{a\alpha}(\Delta\omega^{o}_{a\alpha})d\Delta\omega^{o}_{a\alpha} = \frac{2}{\pi}\,|\mu^{o}_{a\alpha}|^2\, d\Delta\omega^{o}_{a\alpha}\int_0^\infty x\,dx \quad .$$

(5-10b.3)

$$\cdot\,(\Delta\omega^{o}_{a\alpha}\sin\Delta\omega^{o}_{a\alpha}x + \gamma_{a\alpha}\cos\Delta\omega^{o}_{a\alpha}x)\,e^{-(\lambda_{a\alpha}x)^{3/2} - \gamma_{a\alpha}x} \quad .$$

It is now convenient to measure frequencies in units of $\lambda_{a\alpha}$ and to introduce the ratio, R, of $\lambda_{a\alpha}$ and $\gamma_{a\alpha}$. Therefore, R is a measure of the relative importance of ion and electron broadening:

$$\beta \equiv \frac{\Delta\omega^{o}_{a\alpha}}{\lambda_{a\alpha}}$$

(5-10b.4)

$$R \equiv \frac{\lambda_{a\alpha}}{\gamma_{a\alpha}} \quad .$$

If we now make another change of variables in (5-10b.3) by putting $\lambda_{a\alpha}x = y^{2/3}$, then the distribution becomes

$$I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2\,\frac{4}{3}\,\frac{d\beta}{\pi}\int_0^\infty y^{1/3}dy\left(\beta\sin\beta y^{2/3} + \frac{1}{R}\cos\beta y^{2/3}\right)e^{-\left(y + \frac{y^{2/3}}{R}\right)}$$

(5-10b.5)

$$= |\mu^{o}_{a\alpha}|^2\,\frac{4}{3\pi}\,d\beta\;R_e\left(-i\beta + \frac{1}{R}\right)\int_0^\infty y^{1/3}\,dy\;e^{-y^{2/3}\left(\frac{1}{R} - i\beta\right) - y} \quad .$$

Expanding $\exp\,[-y^{2/3}\,(1/R - i\beta)]$ in a power series and integrating term by term yields

$$(5\text{-}10b.6)\quad I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2\,\frac{4}{3\pi}\,d\beta\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\,R_e\left(-i\beta + \frac{1}{R}\right)^n\int_0^\infty dy\;e^{-y}\,y^{\frac{2n-1}{3}} \quad .$$

The integral is given by a gamma function, so for small β we have finally

$$(5\text{-}10b.7)\quad \frac{I_{a\alpha}(\beta)d\beta}{|\mu^{o}_{a\alpha}|^2} = \frac{4}{3}\,\frac{d\beta}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\cdot\Gamma\left[\frac{2}{3}\,(n+1)\right]\cdot\left(\beta^2 + \frac{1}{R^2}\right)^{n/2}\cdot\cos(nt_g^{-1}\beta R) \quad .$$

For the case of zero electron density, $R \to \infty$, so the above series reduces to the well-known Holtsmark expansion

$$\frac{I_{a\alpha}(\beta)d\beta}{|\mu^o_{a\alpha}|^2} = \frac{4}{3\pi} d\beta \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \beta^n \Gamma\left[\frac{2}{3}(n+1)\right] \cos\frac{n\pi}{2}$$

(5-10b.8)

$$= \frac{4}{3\pi} d\beta \left[\Gamma(2)\,\beta^2 - \frac{\Gamma\left(\frac{10}{3}\right)}{6}\beta^4 + \cdots\right] .$$

10c. A Series Expansion for Large Frequencies

If we let $z = \beta y^{2/3}$ in the integral (5-10b.5), then the absorption coefficient can be expressed in another convenient form:

$$(5\text{-}10c.1)\quad I_{a\alpha}(\beta)d\beta = |\mu^o_{a\alpha}|^2 \frac{2}{\pi}\frac{d\beta}{\beta^2}\int_o^{\infty} z\,dz\left(\beta \sin z + \frac{1}{R}\cos z\right) e^{-\frac{z}{\beta R} - \left(\frac{z}{\beta}\right)^{3/2}}$$

Expanding $\exp -(z/\beta)^{3/2}$ in a power series and integrating term by term gives

$$I_{a\alpha}(\beta)d\beta = |\mu^o_{a\alpha}|^2 \frac{2}{\pi}\frac{d\beta}{\beta^2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \frac{1}{\beta^{3(n-1)/2}} \int_o^{\infty} dz \left[z^{\left(\frac{3n+1}{2} - 1\right)} e^{-\frac{z}{\beta R}} \cdot\right.$$

(5-10c.2)

$$\left. \cdot\,(\beta \sin z + 1/R \cos z)\right] .$$

The integral in this expansion can also be expressed in terms of gamma functions:[66]

$$(5\text{-}10c.3)\quad \int_o^{\infty} dz\, z^{k-1}\, e^{-\frac{z}{\beta R}} \begin{pmatrix}\sin z \\ \cos z\end{pmatrix} = \frac{\Gamma(k)}{\left(1 + \frac{1}{(\beta R)^2}\right)^{\frac{k}{2}}} \begin{pmatrix}\sin \\ \cos\end{pmatrix} k\, t_g^{-1}\, \beta R .$$

With (5-10c.3) the absorption coefficient (5-10c.2) becomes

$$I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2 \frac{2}{\pi} d\beta \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \frac{\Gamma\left(\frac{3n+1}{2}\right)}{\beta\left(\frac{3n+1}{2}\right)} \cdot$$

(4-10c.4)

$$\cdot \frac{\beta \sin\left(\frac{3n+1}{2} t_g^{-1} \beta R\right) + \frac{1}{R} \cos\left(\frac{3n+1}{2} t_g^{-1} \beta R\right)}{\left[1 + \frac{1}{(\beta R)^2}\right]^{\frac{3n+1}{4}}} \cdot$$

Using the following identity,

$$\beta R = \frac{\sin\left(t_g^{-1} \beta R\right)}{\cos\left(t_g^{-1} \beta R\right)} , \tag{4-10c.5}$$

one finds

$$\beta \sin\left(\frac{3n+1}{2} t_g^{-1} \beta R\right) + \frac{1}{R} \cos\left(\frac{3n+1}{2} t_g^{-1} \beta R\right) =$$

$$\beta \left[1 + \frac{1}{(\beta R)^2}\right]^{1/2} \cos\left(\frac{3n-1}{2} t_g^{-1} \beta R\right) . \tag{5-10c.6}$$

With this identity, the absorption coefficient becomes finally

$$I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2 d\beta \frac{2}{\pi} \left\{ \frac{1}{R(\beta^2 + 1/R^2)} \right.$$

$$\left. + \sum_{n=2}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \frac{\Gamma\left(\frac{3n+1}{2}\right)}{\beta\left(\frac{3n-1}{2}\right)} \frac{\cos\left(\frac{3n-1}{2} t_g^{-1} \beta R\right)}{\left[1 + 1/(\beta R)^2\right]^{\frac{3n-1}{4}}} \right\} . \tag{5-10c.7}$$

Let us now examine the two limiting cases where either the electron density or the ion density is set equal to zero. For zero electron density $R \to \infty$, and one obtains the usual Holtsmark expansion[6,7]

$$I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2 d\beta \frac{2}{\pi} \sum_{n=2}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} \frac{\Gamma\left(\frac{3n+1}{2}\right)}{\beta\left(\frac{3n-1}{2}\right)} \cos\left(\frac{3n-1}{4} \pi\right) . \tag{5-10c.8}$$

For zero ion density $\beta \to \infty$, so only the first term in (5-10c.7) is non-zero. With the definitions of β and R the first term is given by

$$(5\text{-}10c.9) \qquad I_{a\alpha}(\Delta\omega_{a\alpha}) = \frac{2}{\pi} |\mu^{o}_{a\alpha}|^2 \frac{\gamma_{a\alpha}}{(\Delta\omega^{o}_{a\alpha})^2 + \gamma^2_{a\alpha}} .$$

This is the familiar dispersion line shape to be expected for electron broadening only.

10d. Normalization of the Absorption Coefficient

It is now necessary to discuss the normalization of our distribution function. From (5-10c.1) with $z \equiv \beta p$,

$$(5\text{-}10d.1) \int_0^\infty I_{a\alpha}(\beta)d\beta = |\mu^{o}_{a\alpha}|^2 \frac{2}{\pi} \int_0^\infty\int_0^\infty pdpd\beta \left(\beta \sin \beta p + \frac{1}{R} \cos \beta p\right) e^{-p/R - p^{3/2}} .$$

With a partial integration of the first term twice and the second term once, this becomes

$$(5\text{-}10d.2) \int_0^\infty I_{a\alpha}(\beta)d\beta = - |\mu^{o}_{a\alpha}|^2 \frac{2}{\pi} \int_0^\infty\int_0^\infty d\beta dp \left[\frac{\sin \beta p}{\beta} \frac{d^2}{dp^2} \left(pe^{-p/R - p^{3/2}}\right) + \frac{\sin \beta p}{\beta p} \frac{d}{dp} \left(pe^{-p/R - p^{3/2}}\right)\right] .$$

Since

$$\int_0^\infty d\beta \frac{\sin \beta p}{\beta} = \frac{\pi}{2} , \quad p > 0 ,$$

the integrated absorption coefficient is now

$$(5\text{-}10d.3) \int_0^\infty I_{a\alpha}(\beta)d\beta = - |\mu^{o}_{a\alpha}|^2 \int_0^\infty dp \left(\frac{d^2}{dp^2} + \frac{1}{R} \frac{d}{dp}\right) pe^{-p/R - p^{3/2}}$$
$$= |\mu^{o}_{a\alpha}|^2 \left(\frac{3}{2}\sqrt{p} - 1\right) e^{-p/R - p^{3/2}} \Bigg|_0^\infty ,$$

so that finally

$$\int_0^\infty I_{a\alpha}(\beta)d\beta = |\mu^o_{a\alpha}|^2 \quad , \tag{5-10d.4}$$

and, since the distribution function is an even function of β,

$$\int_{-\infty}^{\infty} I_{a\alpha}(\beta)d\beta = 2|\mu^o_{a\alpha}|^2 \quad . \tag{5-10d.5}$$

It is to be remembered that $|\mu^o_{a\alpha}|^2$ is proportional to the line strength of a single displaced Stark component so that $2|\mu^o_{a\alpha}|^2$ is proportional to the strength of a pair of displaced components. In calculating the frequency distribution in a hydrogen line which is composed of several Stark components, one must, of course, sum over the components, using the distribution function (5-10c.1) or the various series expansions derived earlier:

$$I_{if}(\omega) = \sum_{a\alpha} \rho_\alpha(0)\, I_{a\alpha}(\Delta\omega^o_{a\alpha}) \quad , \tag{5-10d.6}$$

where

$$\int_0^\infty I_{if}(\omega)d\omega = \sum_{a\alpha} 2\, \rho_\alpha(0)\, |\mu^o_{a\alpha}|^2 \quad . \tag{5-10d.7}$$

This is the usual expression for the total absorption coefficient of an unperturbed hydrogen line.

11. The Relative Importance of Ion and Electron Broadening

In this section the theory which takes into account both ion and electron broadening will be compared with the usual Holtsmark theory for ion broadening. For convenience, a set of functions $K_n(\beta R)$ will be introduced. These functions are correction factors to each term in the Holtsmark series (5-10c.8) and have been plotted in Figure 5 for n =

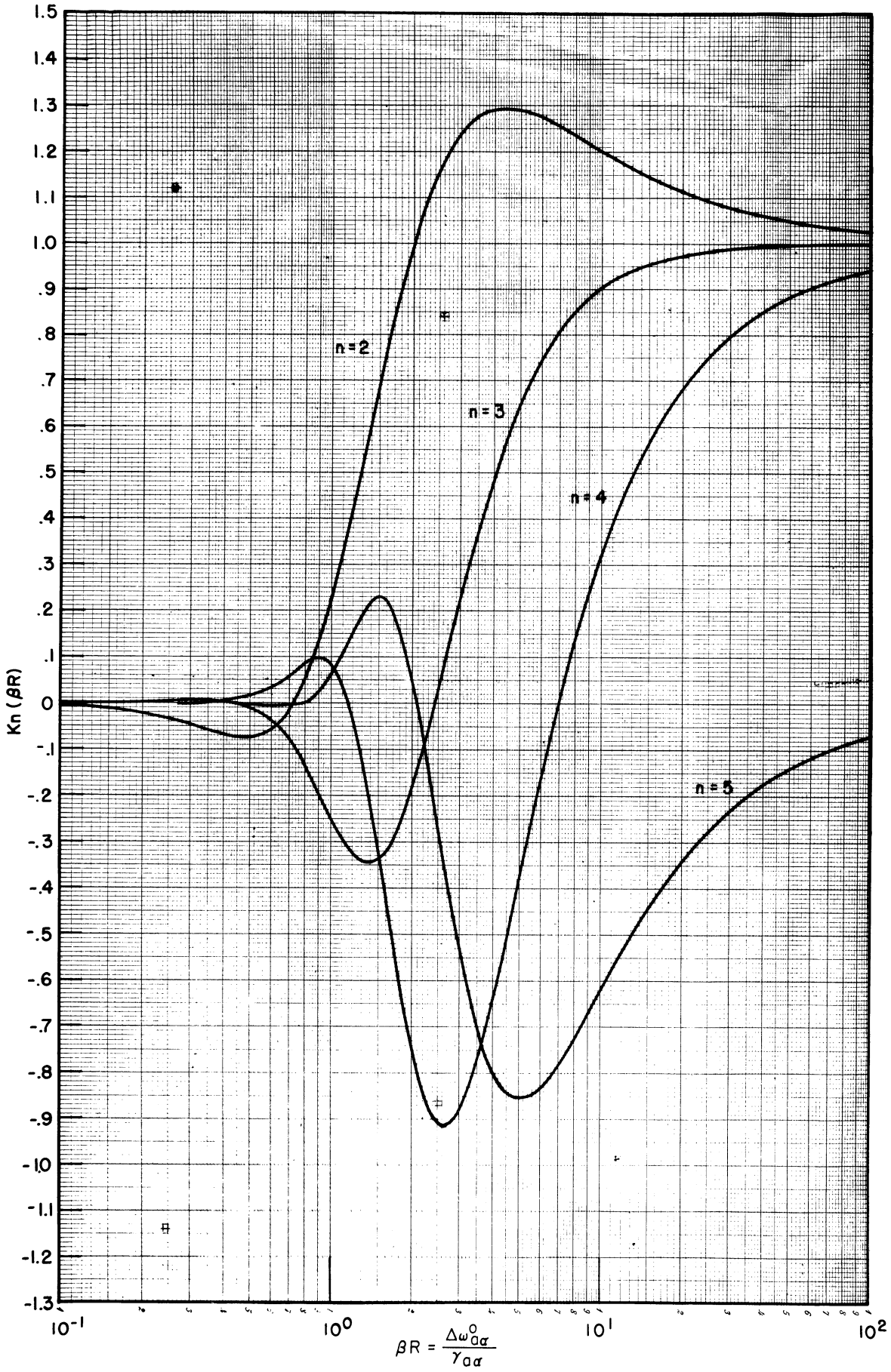


Figure 5. Correction factors $K_n(\beta R)$ to the Holtsmark series for n = 2,3,4,5.

2, 3, 4, 5. They are defined by

$$(5\text{-}11.1a)\quad K_n(\beta R) \equiv \frac{\cos\left(\frac{3n-1}{2}\, t_g^{-1}\, \beta R\right)}{\left(\cos\ \frac{3n-1}{4}\,\pi\right)} \cdot \frac{1}{\left[1+\frac{1}{(\beta R)^2}\right]^{\frac{3n-1}{4}}},$$

for $\cos\left(\frac{3n-1}{4}\,\pi\right) \neq 0$,

$$(5\text{-}11.1b)\quad K_n(\beta R) \equiv \cos\left(\frac{3n-1}{2}\, t_g^{-1}\, \beta R\right) \cdot \frac{1}{\left[1+\frac{1}{(\beta R)^2}\right]^{\frac{3n-1}{4}}},$$

for $\cos\left(\frac{3n-1}{4}\right)\pi = 0$.

The absorption coefficient written in terms of $K_n(\beta R)$ is

$$I_{a\alpha}(\beta)d\beta = \frac{2}{\pi}\,|\mu^o_{a\alpha}|^2\,\frac{R}{(\beta^2R^2+1)}$$

$$+\sum_{n=2}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\cdot\frac{\Gamma\left(\frac{3n+1}{2}\right)}{\beta\left(\frac{3n-1}{2}\right)}\cdot\cos\left(\frac{3n-1}{4}\right)\pi\cdot K_n(\beta R)$$

(5-11.2)

$$\cos\left(\frac{3n-1}{4}\,\pi\right)\neq 0$$

$$+\sum_{n=5}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\cdot\frac{\Gamma\left(\frac{3n+1}{2}\right)}{\beta\left(\frac{3n-1}{2}\right)}\cdot K_n(\beta R)$$

$$\cos\left(\frac{3n-1}{4}\,\pi\right) = 0\ .$$

or

$$\frac{I_{a\alpha}(\beta)d\beta}{|\mu^o_{a\alpha}|^2} = \frac{2}{\pi}\,\frac{R}{(\beta^2R^2+1)} + \frac{2}{\pi}\left[\frac{2.35\,K_2(\beta R)}{\beta^{5/2}} + \frac{12\,K_3(\beta R)}{\beta^4}\right.$$

(5-11.3)

$$\left. + \frac{33.9\,K_4(\beta R)}{\beta^{11/2}} + \frac{210}{\beta^7}\,K_5(\beta R) - + \ldots\right]d\beta\ .$$

In the limit of zero electron density these functions are constants and independent of the frequency:

$$(5\text{-}11.4)\qquad \begin{aligned} K_n(\beta R) &\to 1 \qquad \cos\left(\frac{3n-1}{4}\pi\right) \neq 0 \\ K_n(\beta R) &\to 0 \qquad \cos\left(\frac{3n-1}{4}\pi\right) = 0 \quad . \end{aligned}$$

From the graphs of the functions $K_n(\beta R)$ it is seen that they deviate considerably from their Holtsmark values for $\beta R < 100$ (or for frequencies measured from the line center that are less than 100 times the electron half-width parameter $\gamma_{a\alpha}$).

In addition to the correction factors, $K_n(\beta R)$, to each term in the usual Holtsmark series there is an additional term in the distribution (5-11.2) that depends only on the electron density and has the well-known Lorentzian frequency dependence. This term becomes large on the line wing. In Figure 6 the theory for electron broadening alone, ion broadening alone, and for both electron and ion broadening are compared for the following conditions; $N_e = N_i = 10^{16}$ cm^{-3}, T = 15,000°K, and $X_{a\alpha} = 10$. It was found that the series expansion (5-11.3) for $\beta \geq 5$ was accurate to three significant figures. For $\beta < 5$ the absorption coefficient was calculated by numerically integrating (5-10a.11). In these calculations the nonadiabatic contribution was <u>estimated</u>* by taking the contribution to $\gamma_{a\alpha}$ by the weak collisions to be twice the adiabatic contribution (see 5-6.7):

$$(5\text{-}11.5)\qquad \begin{aligned} (\gamma_{a\alpha})_{weak} &\cong -2\left[\frac{16}{3}\frac{N_e}{\bar{v}_e}(AX_{a\alpha})^2 \ln \tilde{\delta}_m^{a\alpha}\right] \\ (\gamma_{a\alpha})_{strong} &= 2.36\left[\frac{16}{3}\frac{N_e}{v_e}(AX_{a\alpha})^2\right] \\ \gamma_{a\alpha} &= (\gamma_{a\alpha})_{weak} + (\gamma_{a\alpha})_{strong} \quad . \end{aligned}$$

*For Lyman α, the half-width was three times that predicted by the adiabatic theory for electron broadening and it is to be expected that the adiabatic and nonadiabatic contribution to the electron broadening for other hydrogen lines will also be comparable.

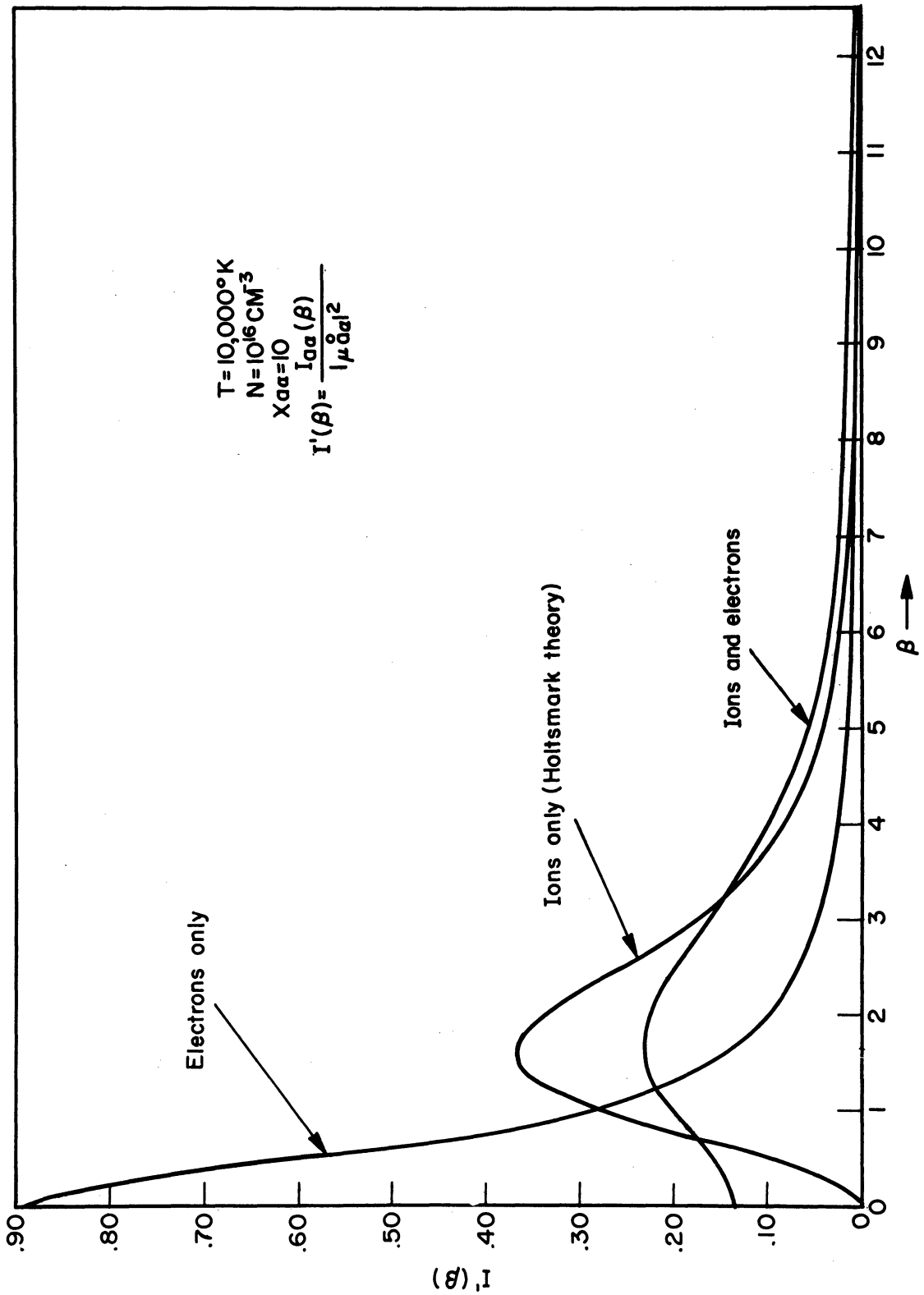


Figure 6. Comparison of the theories for electron broadening, ion broadening, and broadening by both ions and electrons.

The detailed computation of the nonadiabatic contribution to $\gamma_{a\alpha}$ for hydrogen lines other than Lyman α has not yet been completed. It is evident from Figure 6 that the half-width predicted by our theory differs only slightly (21 percent in this case) from that predicted by Holtsmark, even though the frequency distribution is greatly modified by including electrons in the theory. For this reason the experimental determination of the Balmer line half-width is not a sensitive measure of the validity of either theory. Note also from Figure 6 that the position of the Holtsmark maximum does not depend on the electron density. This behavior is borne out experimentally. In Figure 7 an experimentally determined profile* of H_β is compared with the Holtsmark theory. The qualitative features (Figure 6) of our theory agree well with the qualitative features of the experimental profile. In experimental applications, therefore, the measurement of the frequency splitting of the double maxima in H_β or H_δ affords an easy method for the estimation of ion densities in a high-temperature plasma.

The importance of electron broadening can also be demonstrated by examining the limit of (5-10c.7) for large frequencies:

$$(5\text{-}11.6a) \qquad I_{a\alpha}(\beta)d\beta \to \frac{2}{\pi}\,\frac{|\mu^o_{a\alpha}|^2}{\beta^2 R}\left(1 + \frac{R\Gamma\left(\frac{7}{2}\right)\cos\frac{5\pi}{4}}{\sqrt{\beta}}\right)d\beta \quad .$$

With $\beta \equiv \dfrac{\Delta\omega_{a\alpha}}{\lambda_{a\alpha}}$ and $R \equiv \lambda_{a\alpha}/\gamma_{a\alpha}$, this equation can also be written

$$(5\text{-}11.6b) \quad I_{a\alpha}(\Delta\omega_{a\alpha})d\Delta\omega_{a\alpha} = \frac{2}{\pi}\,\frac{|\mu^o_{a\alpha}|^2\gamma_{a\alpha}}{(\Delta\omega^o_{a\alpha})^2}\left(1 + \frac{.707\,\Gamma\left(\frac{7}{2}\right)\lambda_{a\alpha}{}^{3/2}}{\gamma_{a\alpha}\,\Delta\omega^o_{a\alpha}}\right)d\Delta\omega^o_{a\alpha} \quad .$$

*Taken from page 137, Ref. 1.

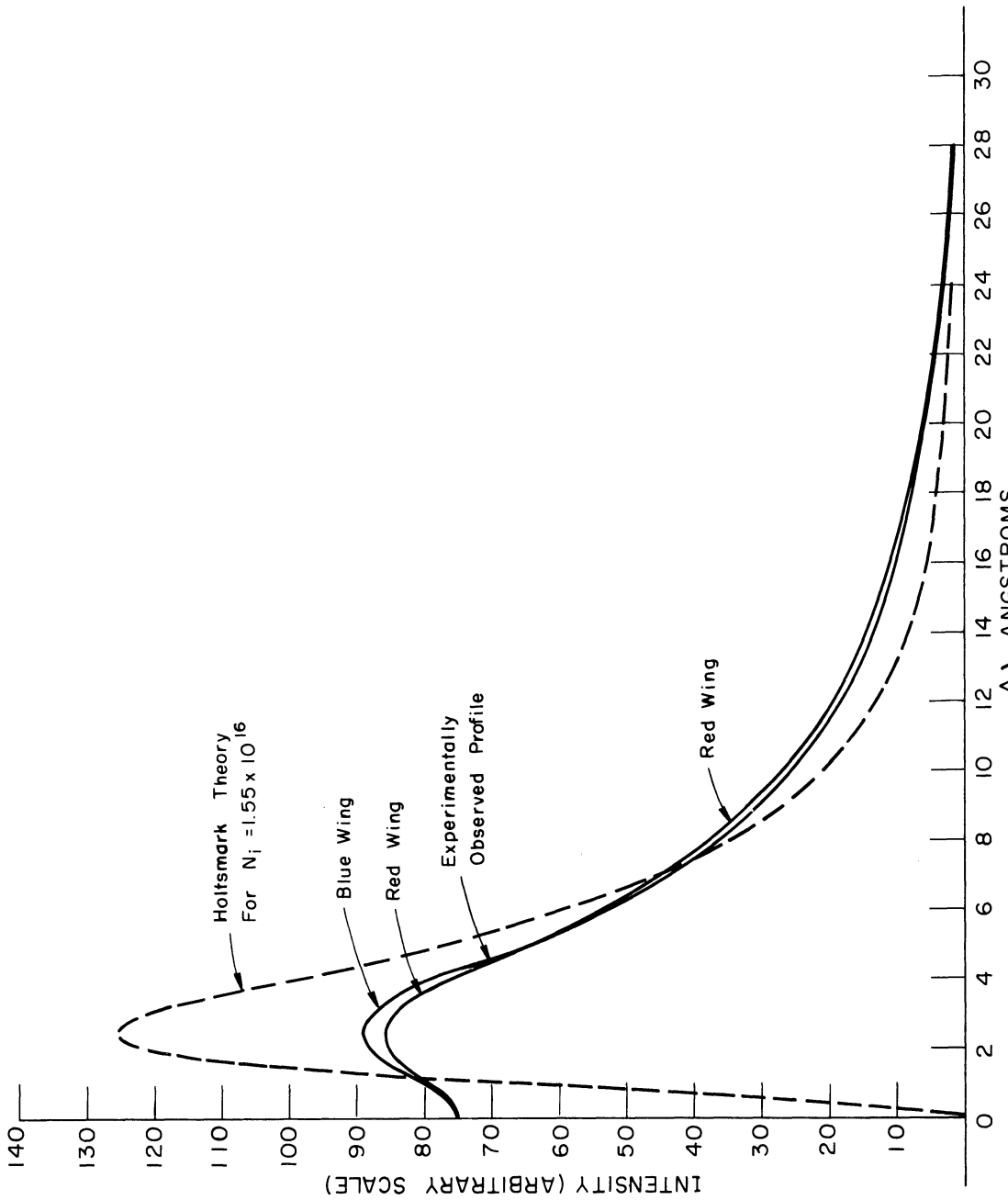


Figure 7. Comparison of the Holtsmark theory with a typical H_β profile obtained in the Michigan shock tube.

In this formula the expression for $\gamma_{a\alpha}$ will also be taken to be that given by (5-11.5) in order to take the nonadiabatic broadening into account approximately.

With the following relations obtained earlier,

$$\lambda_{a\alpha}^{3/2} = 4.21\, N_i\, (AX_{a\alpha})^{3/2}$$

$$\gamma_{a\alpha} \cong \frac{16\, N_e}{3\, \bar{v}_e} (AX_{a\alpha})^2 \,(2.36 - 2\, \ell n\, \tilde{\delta}_m^{a\alpha})$$

$$\tilde{\delta}_m^{a\alpha} = 1.80 \times 10^{-6}\, X_{a\alpha}\, \frac{\sqrt{N_e}}{T} \qquad (5\text{-}11.7)$$

$$\bar{v}_e = 6.215 \times 10^5 \sqrt{T}$$

$$A = \frac{3}{2} \frac{e^2\, a_o}{\hbar} \,,$$

one finds that the distribution (5-11.6b) for large β (on the far wing) becomes

$$I_{a\alpha}(\Delta\omega_{a\alpha}^o) \cong \frac{2}{\pi} \frac{|\mu_{a\alpha}^o|^2 \gamma_{a\alpha}}{(\Delta\omega_{a\alpha}^o)^2} \left[1 + \frac{10^6\, N_i\, T}{N_e\, (X_{a\alpha}\, \Delta\omega_{a\alpha}^o)^{1/2} (2.36 - 2\ell n\, \tilde{\delta}_m^{a\alpha})}\right]. \qquad (5\text{-}11.8)$$

The first term in the above expression depends only on the electron density. The second term is the ratio of the wing intensity due to ion broadening to the wing intensity due to electron broadening. Note that for given frequency and temperature this ratio is independent of the ion density when $N_e = N_i$, except for the slowly varying dependence of $\ell n\, \tilde{\delta}_m^{a\alpha}$ on N_e. This is of importance in the application of this line broadening theory to the study of Balmer line profiles in stellar atmospheres since the wing distribution can generally be used with sufficient accuracy to calculate the profiles. For given $\Delta\omega_{a\alpha}^o$ and temperature the relative im-

portance of ion and electron broadening is essentially independent of the ion density. Therefore, even for the low ion densities encountered in stellar atmospheres, one cannot neglect the electron broadening compared to the ion broadening in calculating the shape of the wide Balmer lines that are observed. The general impression that one gets from a survey of the astrophysical literature is that the electron broadening can be neglected at low ion densities. This conclusion is not justified by the calculations presented in this dissertation. For example, for a gas whose temperature is 15,000°K the second term in (5-11.8) is about 1.5 at 30Å from the line center for the H_γ Balmer line. Therefore, the ion and electron broadening are comparable under these conditions for this line. For the higher series members of the Balmer series the $X_{a\alpha}$ (see Table I) are larger than for H_γ. Therefore, the electron broadening becomes more important since $X_{a\alpha}$ appears in the denominator of (5-11.8), which involves the ratio of ion to electron broadening on the line wing.

It can be seen from the Holtsmark ion broadening theory (5-10c.8) that the absorption coefficient behaves like $\Delta\omega^{-5/2}$ on the wing of the line. Therefore, a log-log plot of the absorption coefficient vs frequency should yield a straight line:

$$(5\text{-}11.9) \qquad (\log I_{a\alpha})_{ions} = -\frac{5}{2} \log \Delta\omega^{o}_{a\alpha} + \text{constant} \quad .$$

On the other hand, the theory involving electron broadening alone predicts that the absorption coefficient behaves like $\Delta\omega^{-2}$ on the wing and yields a slope of two on a log-log plot:

$$(5\text{-}11.10) \qquad (\log I_{a\alpha})_{electrons} = -2 \log \Delta\omega^{o}_{a\alpha} + \text{constant} \quad .$$

The combined theory of electron and ion broadening predicts that the slope

of log-log plot of the absorption coefficient vs frequency should be intermediate between 2 and 2.5. This behavior is borne out experimentally and was also indicated by work of Miss Underhill,[64] who studied the frequency dependence of Balmer line wings observed in B-type stars. In these studies it was found that the slope was generally near 2 and in no case greater than 2.3. From these observations it was concluded that the Holtsmark theory does not adequately represent the process of line formation in B-type stars. The astrophysical results are not to be regarded as a proof of the invalidity of the Holtsmark theory, but serve to confirm the discrepancy between theory and laboratory data.

12. Broadening of the Balmer Lines by Nonadiabatic Electron Collisions

The theoretical results of Section III.15 for transitions between nearly degenerate states are complicated by the presence of exponential factors $\exp i\omega_{ab}\tau$ in the phase integrals $\tilde{C}_{ba}$ (see 3-15.11). In this section criteria for neglecting these exponentials will be obtained.

The $\tilde{C}_{ba}$ involve integrals of the type

$$\int_{-\infty}^{\infty} d\tau \, [H_j(\tau)]_{ab} \, e^{-i\omega_{ab}^{o}\tau} \quad . \tag{5-12.1}$$

For the electron broadening of hydrogen lines, $H_j(\tau)$ is found from (5-3.3):

$$H_j(\tau) = \frac{e^2 r}{(v_k^2\tau^2+\rho_j^2)^{3/2}} \, (\rho_j\mu_j+v_k\mu_k\tau) \quad . \tag{5-12.2}$$

Substituting this expression for $H_j(\tau)$ into (5-12.1) yields the following two integrals:

$$\int_{-\infty}^{\infty} \frac{d\tau \, e^{-i\omega_{ab}^{o}\tau}}{(v_k^2\tau^2+\rho_j^2)^{3/2}} \tag{5-12.3a}$$

$$(5\text{-}12.3b) \qquad \int_{-\infty}^{\infty} \frac{d\tau \cdot \tau \cdot e^{-i\omega_{ab}^{o}\tau}}{(v^2\tau^2+\rho_j^2)^{3/2}}$$

The second integral is identically zero for $\omega_{ab}^{o} = 0$. The integral (5-12.3a) has been evaluated by Foley[32] in terms of Hankel functions, $H_1(i\kappa)$, of the first order with an imaginary argument

$$(5\text{-}12.4a) \qquad \int_{-\infty}^{\infty} \frac{d\tau\, e^{-i\omega_{ab}^{o}\tau}}{(v_k^2\tau^2+\rho_j^2)^{3/2}} = \frac{\pi\, \omega_{ab}^{o}}{\rho_j\, v_k^2}\, H_1\left(\frac{i\rho_j\omega_{ab}^{o}}{v_k}\right) .$$

Similarly, the integral (5-12.3b) is given by

$$(5\text{-}12.4b) \qquad \int_{-\infty}^{\infty} \frac{d\tau \cdot \tau \cdot e^{-i\omega_{ab}^{o}\tau}}{(v_k^2\tau^2+\rho_j^2)^{3/2}} = \frac{\pi i}{\rho_j v_k^2}\, \frac{d}{d\omega_{ab}^{o}}\left[\omega_{ab}^{o}\, H_1\left(\frac{i\rho_j\omega_{ab}^{o}}{v_k}\right)\right] .$$

For large $\rho_j\omega_{ab}^{o}/v_k$, the Hankel function becomes*

$$(5\text{-}12.5) \qquad H_1(i\kappa) \cong \frac{e^{-\kappa}}{\sqrt{\frac{\pi\kappa}{2}}} \; ; \qquad \frac{\rho_j\omega_{ab}^{o}}{v_k} \equiv \kappa \gg 1 .$$

Therefore, the nonadiabatic (off-diagonal matrix elements vanish exponentially with increasing $\rho_j\omega_{ab}^{o}/v_k$. However, for sufficiently high velocities, the collision time, $\tau_d \sim \rho/v$, is small compared to the rate $(\omega_{ab}^{o})^{-1}$ and one may approximate the exponentials exp $i\omega_{ab}^{o}\tau$ in $\tilde{C}_{ba}$ by unity.

If the splitting ω_{ab}^{o} is due to static ion fields, then ω_{ab}^{o} is of the order

$$(5\text{-}12.6) \qquad \omega_{ab}^{o} \sim \lambda_{ab} = 4.52\, X_{ab} N^{2/3} ,$$

where again λ_{ab} is the Stark shift in units of circular frequency that corresponds to the Holtsmark mean field strength (see 4-1.23). The maxi-

*Jahnke-Emde, Tables, pages 137-138, Ref. 65.

mum value of κ for a given density and temperature is of the order

$$(5\text{-}12.7a) \qquad \kappa_m = \frac{\lambda_{ab}\,\rho_m}{\bar{v}} = \frac{.562\,X_{ab}}{e}\sqrt{m_e}\,\frac{N_i^{2/3}}{N_e^{1/2}}\,,$$

where ρ_m is the Debye screening length (5-5.5), $\bar{v}$ is the average electron velocity, m_e and e are the electronic mass and charge, and N_e and N_i are the electron and ion densities. The X_{ab} can be calculated with the definition (4-1.6). For equal ion and electron densities, κ_m becomes

$$(5\text{-}12.7b) \qquad \kappa_m = 3.5 \times 10^{-5}\,X_{ab}\,N^{1/6}$$

For $N = 10^{16}$ ions/cm^3, $\kappa_m = .016\,X_{ab}$. Therefore, κ is small compared to unity for X_{ab} = 1-20 and for impact parameters less than the Debye shielding distance. Thus, one may neglect the exponentials exp $i\omega_{ab}^{o}\tau$ in calculating the electron broadening of the Balmer lines. This simplifies the numerical work immensely since one must average the line profile due to electron broadening over the static ion field splitting. This would involve averages of the Hankel function with the Holtsmark probability distribution if κ were not small compared to unity.

13. Comparison of the Theory with Experiment

An experimental study of the broadening of the Balmer line H_β (4861Å) was carried out by Turner[1,2] and Doherty[2] in the shock-tube laboratory at The University of Michigan. These experiments were described briefly in Chapters II and IV.

The Balmer line H_β was chosen for study for the following reasons:

1. The intensity of the H_β line was high enough so that time-resolved spectra could be obtained, but not so intense as to result on self-absorption. The H_α line was not selected because of self-absorption.

2. The line is isolated from the other Balmer lines so that there is no overlapping. The higher series members of the Balmer series tend to broaden and overlap at high ion densities.

3. There is no central component for H_β (the central components do not exhibit a static Stark effect and our theory for electron broadening is uncertain at the line center).

4. There are relatively few Stark components in H_β, so the theoretical line profiles are comparatively easy to compute.

5. The H_β line lies in a convenient region of the spectrum (4861Å).

The line shape was calculated with the aid of the series expansion (5-10c.7) for $\Delta\omega^o_{a\alpha}$ greater than the H_β half-width. For frequencies smaller than the half-width it was necessary to compute the intensity by numerical integrations of the basic integral expression for $I_{a\alpha}(\Delta\omega^o_{a\alpha})$. The result of these calculations for the wing of H_β is shown in Figure 8, where the theory for ion and electron broadening is compared with the Holtsmark distribution for ion broadening. It is seen that the intensity on the far wings is appreciably greater if the electron broadening is taken into account. The temperatures and ion densities were chosen to conform to typical conditions encountered in the shock tube. These calculations showed that the shape of the distribution is not very sensitive to the temperature.

In Figure 9, where we have compared the Holtsmark theory with a typical H_β profile obtained in the shock tube,* it is shown that the Holtsmark distribution yields too narrow a line, while our theory yields an additional broadening that is of about the right order of magnitude. Further experiments are needed to determine more accurately the wing distri-

*Private communication with E. B. Turner and L. Doherty.

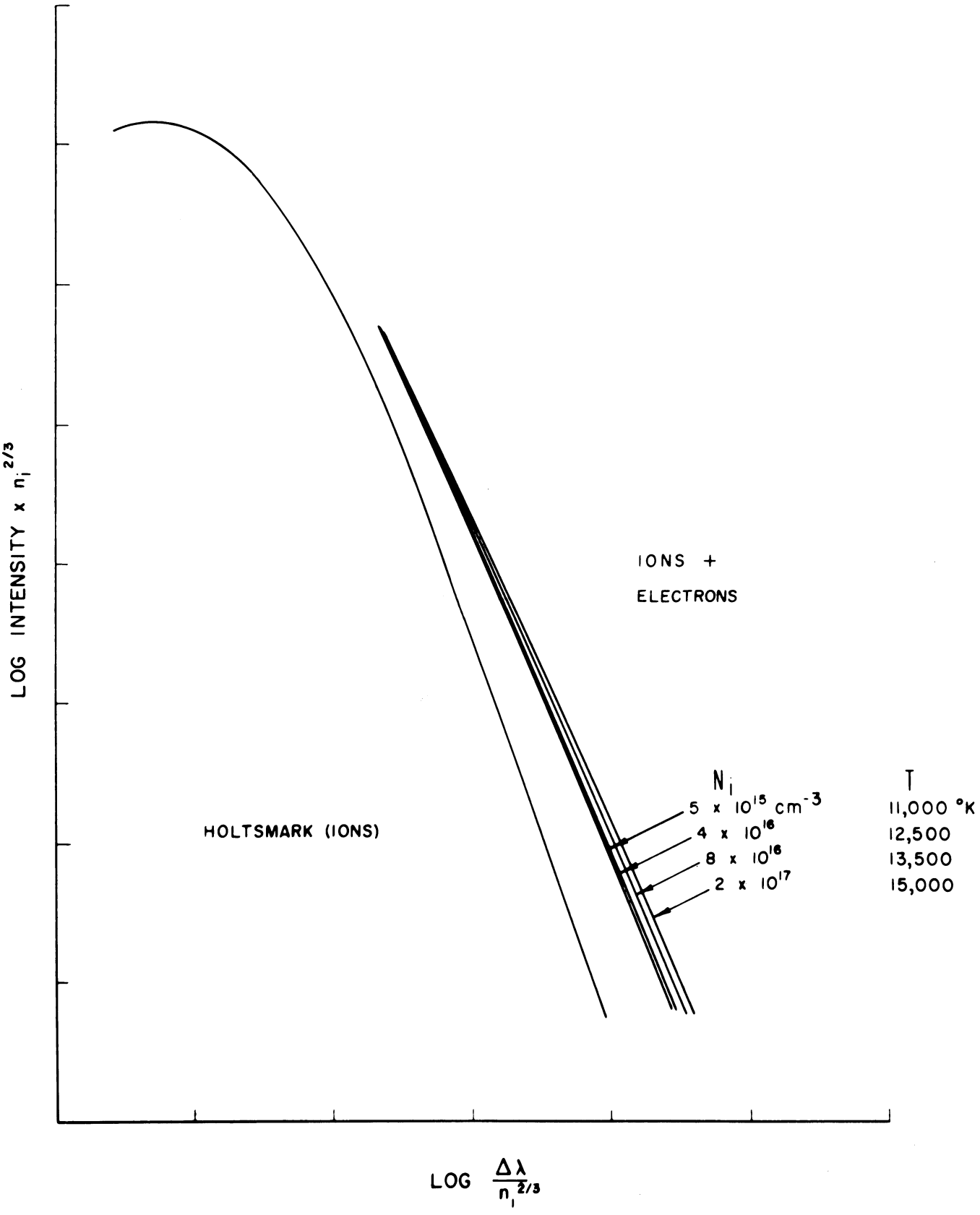


Figure 8. Comparison between the Holtsmark theory and the theory for broadening by both ions and electrons illustrating the density dependence.

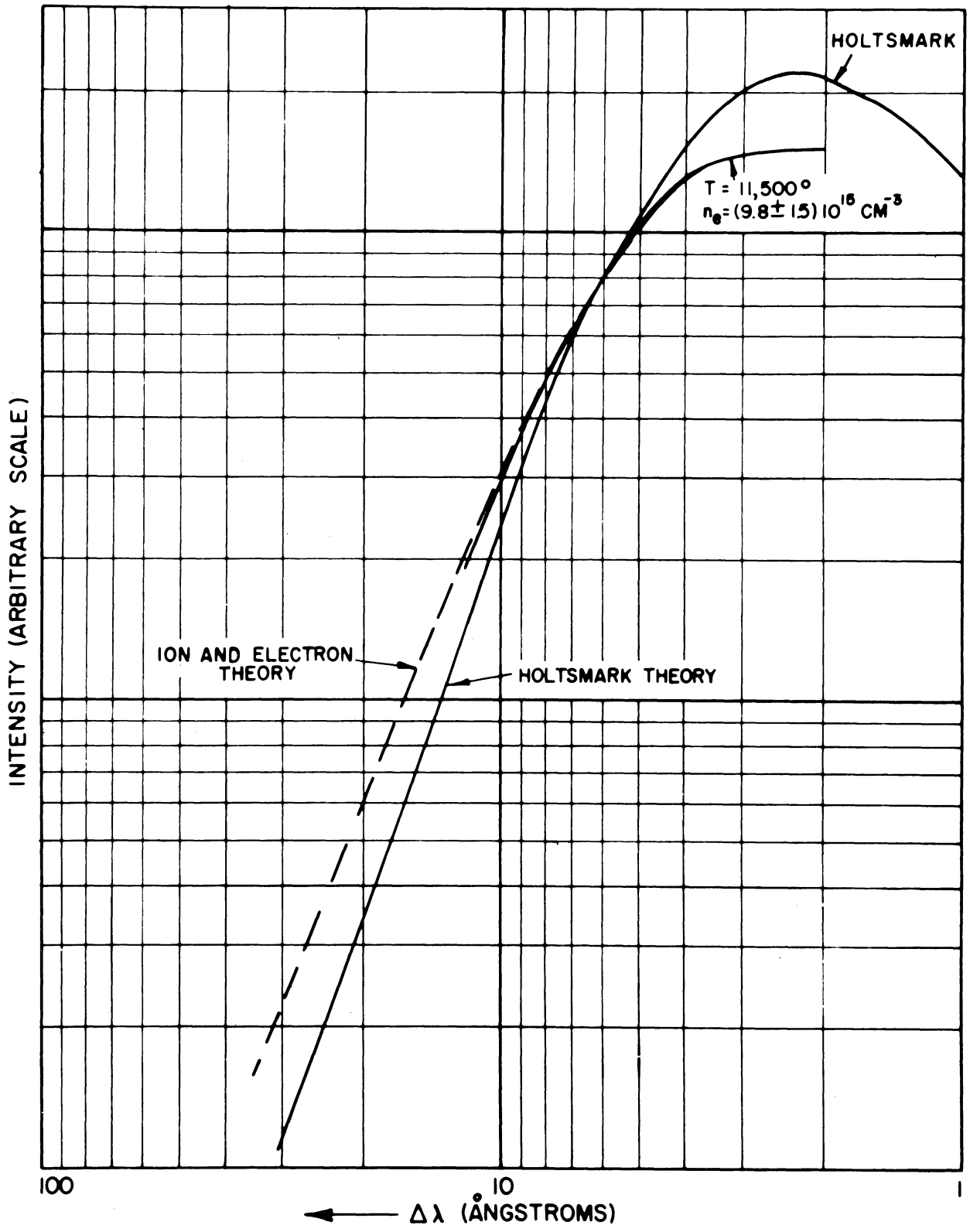


Figure 9. Comparison between the present theory and the Michigan experiments.

bution of Balmer lines other than H_β in the shock tube and to correlate this information with the ion densities and temperatures obtained from hydrodynamic considerations. The good agreement between the theory for ion and electron broadening and the existing experimental data is, however, encouraging. It appears, therefore, that serious errors are introduced into calculations of Balmer line absorption coefficients at all densities by neglecting electron broadening compared to ion broadening.

14. Critique; Some Unsolved Problems

The present theory of hydrogen line broadening by both ions and electrons is not valid near the line center. There are two reasons for this. The nonadiabatic contribution to the electron broadening has been calculated with a perturbation approximation that is not valid for large times and small frequencies, $\Delta\omega$. This approximation restricts the applicability of the theory to frequencies that are large compared to the half-width due to electron broadening. A second source of difficulty in calculating the line profile near resonance is the failure of the statistical theory for small frequencies. Corrections to the statistical theory which take into account the motion of the ions have been calculated by Mrs. Krogdahl.[59] However, it now appears that the statistical assumptions that are implicit in the Krogdahl formalism are probably not correct. Furthermore, the Krogdahl approximation was based on the adiabatic assumption. It is not clear that one can neglect nonadiabatic effects in calculating corrections to the statistical theory.

The theory for electron broadening also suffers from the ad hoc manner in which the close collisions were treated. In reality there is a gradual transition between the strong and weak collision approximations. A theory which takes this transition region into account properly must

avoid the assumption that the amplitudes $|C_{ba}(t)|^2$ are small compared to unity.

Another interesting problem is the simultaneous consideration of both the first- and second-order Stark effects. The quadratic Stark effect will tend to shift the Balmer lines and will probably cause some asymmetry in the frequency distribution.

APPENDIX A

DERIVATION OF THE INTENSITY DISTRIBUTION $I(\omega)$

Let H_o be the Hamiltonian of an unperturbed atom or molecule and let ϕ_n and E_n^o be the wavefunctions and energies of the unperturbed eigenstates of H_o. The ϕ_n and E_n^o then satisfy the stationary Schrödinger equation

$$H_o \phi_n = E_n^o \phi_n \,. \tag{A.1}$$

The Hamiltonian which describes the interaction of the radiating system with the assembly of perturbers is written

$$H(t) = H_o + H_1(t) \,, \tag{A.2}$$

where $H_1(t)$ contains the position coordinates of the perturbers and is time dependent because of their motion. The Schrödinger equation corresponding to $H(t)$ is

$$i\hbar\dot{\psi}_n(t) = H(t)\psi_n(t) \,, \tag{A.3}$$

where the $\psi_n(t)$ are a set of wavefunctions which describe the time development of the perturbed system. A set of initial conditions can now be chosen such that at some time $t=t_o$ the set of wavefunctions $[\psi_n(t)]$ reduces to the unperturbed set $[\phi_n]$

$$\psi_n(t_o) = \phi_n \,. \tag{A.4}$$

Since the ϕ_n are a complete orthonormal set of functions, it follows at once that the $\psi_n(t)$ also form an orthonormal set of functions. To show this, consider two solutions, $\psi_1(t)$ and $\psi_2(t)$, which satisfy the

time-dependent Schrödinger equation (A.3). By the Hermitian character of the Hamiltonian it is clear that

$$(A.5) \qquad i\hbar(\psi_1,\dot{\psi}_2) = (\psi_1,H\psi_2) = (H\psi_1,\psi_2) = -i\hbar(\dot{\psi}_1,\psi_2) .$$

This is equivalent to writing

$$(A.6) \qquad \frac{\partial}{\partial t}(\psi_1,\psi_2) = 0 ,$$

so that the complete set of solutions which are orthonormal at t_o stay orthonormal for all time.

Now let us investigate how the perturbations due to the surrounding assembly of particles affect the optical transition probabilities of the radiating system. The interaction of the radiating atom with the electromagnetic field is

$$(A.7) \qquad H_\ell(t) = -\vec{\mu} \cdot \vec{E}_\omega \cos(\omega t + \alpha) = -\mu E_\omega \cos\theta \cos(\omega t + \alpha) ,$$

where μ is the dipole moment operator, E_ω is the amplitude of the electric field vector, and α is the phase of the light wave. The total Hamiltonian which now includes the radiating system, perturbing particles, and electromagnetic field is

$$(A.8) \qquad H_T(t) = H(t) + H_\ell(t) = H_o + H_1(t) + H_\ell(t) ,$$

and the wavefunction $\psi(t)$ which describes this system satisfies the time-dependent Schrödinger equation

$$(A.9) \qquad i\hbar\dot{\psi}(t) = H_T(t)\psi(t) .$$

It is now convenient to expand $\psi(t)$ in terms of the set of functions* $\psi_n(t)$:

*These wavefunctions are referred to as "collision smeared" wavefunctions in the terminology of Bloom and Margenau.[13]

$$\psi(t) = \sum_n A_n(t)\gamma_n(t) \,. \tag{A.10}$$

Substitution of this expression for $\psi(t)$ into the Schrödinger equation (A.9) yields an equation for the expansion coefficients

$$i\hbar\, \dot{A}_n(t) = \sum_m (H_\ell)^c_{nm}\, A_m(t) \,, \tag{A.11}$$

where $(H_\ell)^c_{nm} \equiv [\gamma_n(t),\, H_\ell(t)\gamma_m(t)]$. The superscript c refers to matrix elements between the "collision smeared" states $\gamma_n(t)$ (not the stationary states ϕ_n). $A_n(t)$ can now be expanded by the well-known iteration procedure. Integrating (A.11) yields

$$A_n(t) = A_n(t_o) + \frac{1}{i\hbar}\int_{t_o}^{t} dt \sum_m (H_\ell)^c_{nm}\, A_m(t_1) \,. \tag{A.12}$$

Similarly,

$$A_m(t_1) = A_m(t_o) + \frac{1}{i\hbar}\int_{t_o}^{t_1} dt_2 \sum_p (H_\ell)^c_{mp}\, A_p(t_2) \,. \tag{A.13}$$

Putting $A_m(t_1)$ into the right-hand side of (A.12) gives directly

$$\begin{aligned} A_n(t) &= A_n(t_o) + \frac{1}{i\hbar}\sum_m \int_{t_o}^{t} dt_1\, [H_\ell(t_1)]^c_{nm}\, A_m(t_o) \\ &+ \frac{1}{(i\hbar)^2}\sum_m \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 \sum_p [H_\ell(t_1)]^c_{nm}\, [H_\ell(t_2)]^c_{mp}\, A_p(t_2) \,. \end{aligned} \tag{A.14}$$

Let $A(t_s)$ and $H^c_\ell(t_s)$ be matrices whose elements are $A_n(t_s)$ and $[H_\ell(t_s)]^c_{nm}$, respectively. In matrix equation form (A.14) becomes

$$\begin{aligned} A(t) &= A(t_o) + \frac{1}{i\hbar}\int_{t_o}^{t} dt_1\, H^c_\ell(t_1)A(t_o) \\ &+ \frac{1}{(i\hbar)^2}\int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2\, H^c_\ell(t_1)H^c_\ell(t_2)A(t_2) \,. \end{aligned} \tag{A.15}$$

Repeating this iteration procedure finally yields

$$A(t) = [1 + \sum_{s=1}^{\infty} R^s(t)]A(t_o) \tag{A.16}$$

or

$$A_n(t) = A_n(t_o) + \sum_{s=1}^{\infty} \sum_m R^s_{nm}(t)\, A_m(t_o) ,$$

where the time-development matrix $[1 + \sum_s R^s(t)]$ is defined by

$$1 + \sum_s R^s(t) = 1 + \sum_s \frac{1}{(i\hbar)^s} \int_{t_o}^{t} dt_s \int_{t_o}^{t_s} dt_{s-1} \cdots \int_{t_o}^{t_1} dt\, [H^c_\ell(t_s) \cdots H^c_\ell(t_1) . \tag{A.17}$$

The probability that at time t the radiating system is in a collision smeared state described by $\psi_n(t)$ is given by the absolute value squared of the quantum mechanical amplitudes $A_n(t)$. From (A.16) these probabilities are

$$\begin{aligned} |A_n(t)|^2 - |A_n(t_o)|^2 &= \sum_s |A_n(t_o)|^2 [R^s_{nn}(t) + R^{s*}_{nn}(t)] \\ &+ \sum_m |A_m(t_o)|^2 \sum_{rs} R^s_{nm}(t)\, R^{r*}_{nm}(t) \\ &+ \sum_s \sum_m{}' A^*_n(t_o) A_m(t_o)\, R^s_{nm}(t) \\ &+ \sum_s \sum_m{}' A^*_m(t_o) A_n(t_o)\, R^{s*}_{nm}(t) \\ &+ \sum_m{}' \sum_p A^*_p(t_o) A_m(t_o) \sum_{rs} R^s_{nm}(t)\, R^{r*}_{nm}(t) . \end{aligned} \tag{A.18}$$

The first sum in this expression can be simplified by making use of the unitary property of the time-development matrix $[1 + \sum_s R^s(t)]$:

$$[1 + \sum_s R^s(t)]^\dagger \, (1 + \sum_r R^r) = 1 ,$$

so that

$$\sum_s (R^{s\dagger} + R^s) = -\sum_{rs} R^{s\dagger} R^r . \tag{A.19}$$

Then, for the diagonal elements one has

$$\sum_s (R^{s\dagger}_{nn} + R^s_{nn}) = -\sum_{rs} \sum_m R^{s\dagger}_{nm} R^r_{mn} \tag{A.20}$$

or

$$\sum_s (R^{s\dagger}_{nn} + R^s_{nn}) = -\sum_{rs} \sum_m R^{s*}_{mn} R^r_{mn} . \tag{A.21}$$

Using this relation (A.18) becomes

$$|A_n(t)|^2 - |A_n(t_o)|^2 = \sum_m |A_m(t_o)|^2 \sum_{rs} R^s_{nm}(t) R^{r*}_{nm}(t)$$

$$-\sum_m |A_n(t_o)|^2 \sum_{rs} R^{s*}_{mn}(t) R^r_{mn}(t) \tag{A.22}$$

$$+ \text{ nondiagonal terms in } A^*_n(t_o)A_m(t_o).$$

Now $R^s(t)$ is of order s in $H_\ell(t)$ according to (A.17), so it is also of order s in the electric field strength E_ω. Therefore, up to order E^2_ω, (A.22) involves only $R^1(t)$ and reduces to

$$|A_n(t)|^2 - |A_n(t_o)|^2 = \sum_m |A_m(t_o)|^2 |R^1_{nm}(t)|^2 - |A_n(t_o)|^2 |R^1_{mn}(t)|^2$$

$$+ \sum_m{}' [A^*_n(t_o)A_m(t_o)R^1_{nm}(t) + A^*_m(t_o)A_n(t_o)R^{1*}_{nm}(t)] \tag{A.23}$$

$$+ \sum_m{}' \sum_p{}' A^*_p(t_o)A_m(t_o)|R^1_{nm}|^2 .$$

With the usual assumption that the phases of the quantum mechanical amplitudes $A_m(t_o)$ of the unperturbed eigenvalues of H_o are randomly distributed in a thermal ensemble, it follows that the density matrix $\overline{\overline{A_n(t_o)A_m(t_o)}} \equiv \rho_{nm}(t_o)$ is diagonal when averaged over the ensemble

$$\rho_{mn}(t_o) = \rho_n(t_o)\, \delta_{mn} . \tag{A.24}$$

Anderson, Bloom, and Margenau *et al.* take $\rho_n(t_o)$ to be the Boltzmann distribution corresponding to the unperturbed eigenstates of H_o:

$$(A.25) \qquad \rho_n(t_o) = \frac{e^{-E_n^o/kT}}{Z(T)} \quad , \quad Z(T) = \sum_m e^{-E_m^o/kT} \quad .$$

This assumption leads to certain difficulties which are examined in Chapter III, Section 8. With the assumption of random phases, the transition probabilities per unit time are now

$$(A.26) \qquad \frac{\overline{\overline{|A_n(t)|^2 - |A_n(t_o)|^2}}}{t-t_o} = \frac{1}{t-t_o} \sum_m [\rho_m(t_o) - \rho_n(t_o)] \, \overline{\overline{|R^1_{nm}(t)|^2}} \quad ,$$

where, according to (A.17) and (A.7), $R^1_{nm}(t)$ is given by

$$(A.27) \qquad R^1_{nm}(t) \equiv \frac{E_\omega \cos\theta}{\hbar} \int_{t_o}^{t} dt_1 \mu^c_{nm}(t_1) \cos(\omega t_1 + \alpha) \quad ,$$

where $\mu^c_{nm}(t) \equiv (\chi_n(t), \mu\chi_m(t))$.

Let us now fix our attention on a particular term in the expression (A.26) for the transition probabilities. For matter in thermal equilibrium with a radiation field, the averaging process indicated by the double bar includes an average over the random phase angle α, the amplitude squared of the electric field vector E_ω^2, and the square of the direction cosine, $\cos^2\theta$. This averaging process yields

$$(A.28) \qquad |R^1_{nm}(t)|^2 = \overline{\overline{\frac{E_\omega^2 \cos^2\theta}{4\hbar^2}}} \left[\left| \int_{t_o}^{t} dt_1 \mu^c_{nm}(t_1) e^{-i\omega t_1} \right|^2 + \left| \int_{t_o}^{t} dt_1 \mu^c_{nm}(t_1) e^{+i\omega t_1} \right|^2 \right] ,$$

where $\overline{\overline{\cos^2\theta}} = 1/3$.

Now for a thermal radiation field the energy density $B_\omega(T)$ is given by

$$(A.29) \qquad B_\omega(T) = \frac{\overline{\overline{|\vec{E}_\omega|^2 + |\vec{H}_\omega|^2}}}{8\pi} = \frac{\overline{\overline{|\vec{E}_\omega|^2}}}{4\pi} = \frac{\overline{\overline{E_\omega^2 \cos^2(\omega t + \alpha)}}}{4\pi} = \frac{\overline{\overline{E_\omega^2}}}{8\pi} \quad ,$$

where $B_\omega(T)$ is given by the Planck distribution,

(A.30) $$B_\omega(T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{(\exp^{\hbar\omega/kT} - 1)} .$$

The total transition probability, using equations (A.29), (A.30), (A.28), and (A.26), is then

$$\frac{|A_n(t)|^2 - |A_n(t_o)|^2}{t-t_o} = \frac{2}{3} \frac{\omega^3}{\pi c^3} \frac{1}{(\exp \frac{\hbar\omega}{kT} - 1)} \frac{1}{(t-t_o)} .$$

(A.31) $$\cdot \sum_m [\rho_m(t_o) - \rho_n(t_o)] \left[\left| \int_{t_o}^{t} dt_1 \mu^c_{nm}(t_1) e^{-i\omega t_1} \right|^2 + \left| \int_{t_o}^{t} dt_1 \mu^c_{nm}(t_1) e^{+i\omega t_1} \right|^2 \right]_{Avg} .$$

The energy radiated and absorbed per second $I(\omega)$ due to transitions which populate and depopulate the state n is given by the product of the photon energy $\hbar\omega$ and the total transition probability (A.31) after a time long enough so that a transition has taken place

(A.32) $$I(\omega) = \hbar\omega \lim_{T\to\infty} \frac{1}{T} \cdot [|A_n(T)|^2 - |A_n(0)|^2] ,$$

or

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \frac{1}{(e^{\hbar\omega/kT} - 1)} \left\{ \sum_m [\rho_m(0) - \rho_n(0)] \lim_{T\to\infty} \frac{1}{T} \cdot \right.$$

(A.33) $$\left. \left[\left| \int_o^T \mu^c_{nm}(t) e^{-i\omega t} dt \right|^2 + \left| \int_o^T \mu^c_{nm}(t) e^{+i\omega t} dt \right|^2 \right] \right\}_{Avg} .$$

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