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RADIATION ABSORPTION PHENOMENA IN GASES

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Berkeley, California
RADIATION ABSORPTION PHENOMENA IN GASES

Bandel Bezzerides
(Ph.D. Thesis)

January 1, 1966
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RADIATION ABSORPTION

PHENOMENA IN GASES

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January 1, 1966

ABSTRACT

Green's function techniques are used to develop a general theory of line broadening in gases. As an example, the impact theory of Baranger et al is derived, including effects due to recoil of the emitting atom. The fundamental processes responsible for the detailed structure of the absorption line are exhibited with the aid of a generalized optical theorem for scattering from thermal systems. To the extent to which intuitive notions of scattering theory are applicable, it is possible to define partial absorption rates corresponding to overall coherent scattering processes. In particular, the fluorescence and quenching of an atom excited by resonance radiation are defined precisely, and a simple formula is given for the branching ratio between these two de-excitation channels.
I. INTRODUCTION

The study of absorption and emission line shapes provides a convenient diagnostic tool for systems which otherwise resist detailed observation. For example, the stellar composition of the universe itself is investigated solely from the emitted radiation. The plasma state offers another important example. Even though large-scale terrestrial plasmas are now available, absorbed and emitted light is still an excellent non-interfering problem, resulting in information necessary to the understanding of the dynamics of the plasma. Finally, the study of intermolecular forces benefits from line shape work in neutral gases.

The kinds of information which one may obtain fall into the broad classification of either kinetic or dynamic depending on whether either Doppler shifting or pressure broadening predominates. Doppler broadening may reveal mass motion and sometimes temperatures, whereas all the possible collisions that the atom can experience contribute to pressure broadening. For all practical purposes broadening due to radiative reaction may be ignored except in situations of high power level.

It is convenient to focus attention specifically on the absorption line to obviate any question concerning the means of excitation of the emitting atoms. A prototype experimental situation would be to scatter radiation from a target composed of a low density collection of atoms A imbedded in a foreign gas B. Then the measured absorption rate as a function of the frequency of
the incident radiation is precisely what is meant by the absorption line shape. From the viewpoint of scattering theory the photons have a number of final channels open to them, and one might expect that the detailed development of the line is established by the competition of these various channels for the incident radiation. That is, the total absorption rate may be regarded as the sum of partial rates each one of which corresponding to an overall coherent scattering process defined by the initial photon flux and one of the final channels.

These partial rates may themselves be of central interest. Thus processes such as resonance fluorescence, etc., should find their analytic expression in such partial rates. It is the purpose of this thesis to construct such partial rates descriptive specifically of resonance fluorescence and the quenching of resonance radiation when broadening due to collisions is significant.

The paper is arranged in such a way that the reader interested only in total rate calculations may restrict attention to the first half of the work. In section II the basic field operators for an interacting gas of absorbing atoms and perturbers are listed, and the total absorption rate is defined. In section III a temperature propagator formalism useful in quantum statistical mechanics is briefly outlined, and the rules for calculating the absorption rate are given. Section IV contains an example calculation for the total absorption rate in the impact approximation including recoil effects. In section V the definition of partial rates for gas collision processes initiated by the absorption of
resonance radiation is considered. The method is motivated by a simple example whereas the details are developed in an appendix. Section VI is devoted to fluorescence and quenching. The relationship to an associated beam experiment is also discussed. Finally, an example calculation is considered for a hydrogen plasma.
II. FUNDAMENTAL EQUATIONS AND DEFINITIONS

The Hamiltonian operator for the system may be written:

\[ H = H_m + H_R + H_I \]  \hspace{1cm} (2.1)

where in second quantization notation

\[ H_m = \sum_{\alpha} \int \psi^+_\alpha(x,t)(E_{\alpha} - \frac{\hbar^2}{2m} \nabla^2_x)\psi_\alpha(x,t) d^3x \]

\[ + \sum_{\alpha \beta} \int d^3x d^3x' \psi^+_\alpha(x,t) \psi_\beta(x',t) \nabla_x \psi_\alpha(x) \frac{\Phi^+(x,t)}{\sqrt{\rho(x,t)}} \frac{\Phi(x,t)}{\sqrt{\rho(x,t)}} \]

\[ + \int \psi^+_\alpha(x,t)(-\frac{\hbar^2}{2m}) \nabla^2_x \psi_\alpha(x,t) d^3x + \frac{i}{\hbar} \int d^3x d^3x' \rho(x,t) V(x-x') \rho(x',t) \]

\[ - \frac{1}{2} N V(0) \]

\[ H_R = \frac{1}{\hbar} \int d^3x \left( \frac{\nabla^2_x}{2}(\psi^+_\alpha(x,t) + \psi^+_\alpha(x,t)) \right) \]  \hspace{1cm} (2.3)
Here $\psi_\alpha(x,t)$ is a field operator in the Heisenberg picture for absorbing atoms of mass $M$ with c.m. position $x$ in an internal state labeled by $\alpha$ of energy $e_\alpha$. $\rho_\alpha(x,t)$ is just the density operator for the atoms in the $\alpha$th state. Similarly $\phi(x,t)$ is the field operator for the foreign gas. For simplicity these atoms have been assumed structureless with an associated density operator $\rho(x,t)$. This restriction may be removed later if desired. These gas particles interact among themselves through a two-body potential $V(x - x')$ and with absorbing atoms through $V_\alpha(x - x')$ or in the coordinate representation through $V(x, z_1, \ldots, z_n, x')$, $z_1, \ldots, z_n$ electron coordinates.

The electric and magnetic field operators $E_{\alpha}(x,t)$ and $B(x,t)$ are obtained from the vector potential field operator $A(x,t)$ which satisfies the transverse gauge condition,

$$\nabla \cdot A(x,t) = 0$$

(2.5)

The atomic current field operator is defined by
\[ \mathcal{J}(\mathbf{x}, t) = \sum_{\kappa, \nu} \psi_{\kappa}^{+}(\mathbf{x}, t) \langle \alpha' | e_{\kappa} | \alpha \rangle \psi_{\alpha}(\mathbf{x}, t) \]  

(2.6)

where

\[ P = \sum_{\kappa=1}^{\nu} P_{\kappa} \]

is the total momentum operator for the atom's electrons.

The matter field operators obey anticommutation relations for equal time arguments,

\[ [\phi^{+}(\mathbf{x}', t), \phi(\mathbf{x}, t)] = 0, \quad [\phi^{+}(\mathbf{x}', t), \phi^{+}(\mathbf{x}, t)] = \delta^{(3)}(\mathbf{x}-\mathbf{x'}) \]  

(2.7)

\[ [\psi_{\kappa}^{+}(\mathbf{x}', t), \psi_{\kappa}(\mathbf{x}, t)] = 0, \quad [\psi_{\kappa}^{+}(\mathbf{x}', t), \psi_{\kappa}(\mathbf{x}, t)] = \delta_{\kappa} \delta^{(3)}(\mathbf{x}-\mathbf{x'}) \]  

(2.8)

Whether the matter is represented by Bose or Fermi fields is unimportant since degenerate systems will not be considered here.

The result of Fourier analyzing the vector potential is:
The $A_\alpha$ satisfy the following commutation relations:

$$[a_\alpha(k), a_\alpha^+(k')] = \Delta_{\alpha\beta}(k) \delta'''(k-k').$$  \hspace{1cm} (2.10)

where

$$\Delta_{\alpha\beta}(k) = \frac{\delta_{\alpha\beta} - \frac{k_x k_y}{k^2}}{k^2}.$$

Upon switching on a macroscopic external field $A^\alpha(X,t)$, the Heisenberg picture for $H$ becomes the interaction picture for $H' = H + H'_I$, where

$$H'_I = -\frac{i\hbar}{2} \int d^3x \, \mathcal{J}(X,t) \, A^\alpha(X,t).$$ \hspace{1cm} (2.11)

The time dependence of $A^\alpha(X,t)$ is fixed by external charges.

If the system was in an eigenstate $|n\rangle$ of $H$ in the distant past, the probability amplitude for transition to state $|m\rangle$ in the far future is given by $\langle n | S(\infty, -\infty) | m \rangle$, where

$$S(t,t_0) = T \exp \left\{ -\frac{i\hbar}{\hbar} \int_{t_0}^{t} dt' \, H'_I(t') \right\}.$$ \hspace{1cm} (2.12)
Thus in the lowest non-vanishing order in the external field, the probability/time for excitation of the system from \( |n\rangle \) to \( |m\rangle \) with energies \( E_n \) and \( E_m \) and momentum \( P_n \) and \( P_m \) by absorption of a photon from the external field becomes:

\[
\Omega \frac{2 \pi \hbar}{\mathcal{N}} \sum_{\xi} \int d^3 k \frac{1}{\mathcal{K} c} |<m | \hat{J}(0) \hat{\xi} | n \rangle|^2 |A_{\xi}^{\ast}(k)|^2 \\
x 2 \pi \hbar \delta(E_m - E_n - \mathcal{K} c) (2\pi \hbar)^3 \delta(P_m - P_n - \mathcal{K} k).
\]

\( \Omega \) is the volume of the system and the c-numbers \( A_{\xi}(k) \) are the expansion coefficients of the external field in plane waves of definite polarization,

\[
A_{\xi}(x,t) = (\hbar^2 c^2)^{1/2} \sum_{\xi} \left[ A_{\xi}^{\ast}(k) e^{i(k \cdot x - \mathcal{K} c t)} + A_{\xi}(k) e^{-i(k \cdot x - \mathcal{K} c t)} \right].
\]

The normalization is chosen in such a way that the time-averaged Poynting vector \( \mathcal{S} = c/4\pi E \times B \) is given by:

\[
\langle \mathcal{S} \rangle = c \mathcal{K} (\hbar c) \langle A_{\xi}^{\ast}(k) \rangle \Omega
\]

identifying
\[ I_\omega^\kappa(k,\omega) = \frac{\omega^{-\kappa} \frac{1}{(2\pi)^3} |\Lambda_\omega^\kappa(k)|^2}{A_\omega^\kappa(k)} \]  

(2.16)

as the flux of photons per unit frequency interval per steradian.

It is convenient to introduce an absorption cross-section defined as the transition rate per unit volume per unit flux of photons of specified momentum and polarization. From Eq. (2.13),

\[ \sigma_\omega^\kappa(k,\omega) = (\omega \epsilon)^\kappa \sum_{n,m} \rho_n |\langle m | J(\omega) | n \rangle|^2 \]

\[ \times 2\pi \delta(E_n-E_m+\hbar\omega)(2\pi \hbar)^2 \delta(-P_m+\vec{p}_n+\hbar \kappa) \]  

(2.17)

where an average over a statistical distribution of initial states is taken through the sum against \( \rho_n \). If the target is regarded as a giant molecule with an associated spectrum of eigenstates, Eq. (2.17) is merely an expression of Fermi's "Golden Rule" in quantum perturbation theory.

A Hamiltonian formulation of quantum mechanics yields probability amplitudes directly, not probabilities. However, an amplitude closely related to the above probability of absorption may be constructed. In fact, that such an associated amplitude exists is essentially the content of the Fluctuation-Dissipation theorem. The absorption rate is in the nature of a dissipative quantity, and it is a type of current autocorrelation
function of the atoms which is a measure of the associated fluctuation. This amplitude will be defined in the following section and the method of its calculation described.
III. PROPAGATOR FORMALISM

A. Spectral Representations

It was noted in the last section that the absorption rate is closely related to an amplitude for which a well defined calculational procedure exists. Consider the retarded current commutator,

\[ \tilde{\Phi}^R_{ij}(x-x',t-t') = i \eta_+(t-t') \left\langle \left[ \mathcal{J}_i(x,t), \mathcal{J}_j(x',t') \right]_+ \right\rangle \tag{3.1} \]

where the Heaviside function

\[ \eta_+(t-t') = \begin{cases} 1 & t > t' \\ 0 & t < t' \end{cases} \]

The brackets indicate a trace over a grand canonical ensemble distribution function,

\[ \rho = \exp(-\mathcal{H} - \mu_\gamma \mathcal{N}) \tag{3.2} \]

\( \Omega \) is the grand potential and \( \mu_\gamma \) the chemical potential for species \( \gamma \). As indicated \( \tilde{\Phi}^R_{ij} \) is only a function of difference variables \( (x-x') \) and \( (t-t') \), and thus may be Fourier analyzed directly. It is a simple matter to show that the associated Fourier coefficients \( \tilde{\Phi}^R_{ij}(\mathcal{P},\omega) \) have the spectral representation,
\[
\Phi^{\mathcal{R}}_{ij}(p) = \int \frac{d\omega'}{2\pi} \left[ \omega - \omega' + i\epsilon \right]^{-1} (e^{i\theta \cdot \omega'}) A_{ij}(p, \omega') 
\]  

where the spectral function

\[
A_{ij}(p, \omega) = \sum_{n, m} e^{i(p-n) \cdot \omega} 2\pi \delta(\omega - E_m + E_n) 
\]

But aside from a constant factor this is precisely the total absorption rate. Thus if $\Phi^{\mathcal{R}}_{ij}$ is known, $A_{ij}$ and hence the total absorption rate are determined. Rather than working directly with $\Phi^{\mathcal{R}}_{ij}$, however, it is convenient to introduce another current function which is simply related to $\Phi^{\mathcal{R}}_{ij}$, but which has the added feature of being in the form of a one-particle propagator. Such propagators may be calculated within the framework of a diagrammatic perturbation theory.

Consider the function

\[
\bar{F}^{\mathcal{R}}_{ij}(X_j, X_j, \tau_1, \tau_2) = \langle T_{\tau_1} \bar{J}_i(X_i, \tau_1) \bar{J}_j(X_j, \tau_2) \rangle  
\]  

where

\[
T_{\tau} \bar{J}_i(X, \tau) \bar{J}_j(X, \tau) = \begin{cases} 
\bar{J}_i(X, \tau) \bar{J}_j(X, \tau) & \tau > \tau_j \\
\bar{J}_j(X, \tau) \bar{J}_i(X, \tau) & \tau < \tau_j 
\end{cases}
\]
That is, \( T \) denotes the usual Wick ordering with the \( J \)'s acting like Bose operators.

\[
J_i(x, \tau) = e^{i\tau/\hbar} J_i(x, 0) e^{-i\tau/\hbar}
\]

(3.6)

To complete the definition \( \tau \) and \( \tau' \) are limited to the domain \([0, \hbar \beta] \). \( \varphi_{ij} \) is then well-defined if absolute convergence for real times is assumed.

Directly from the cyclic invariance of the trace,

\[
\overline{\varphi}_{ij}(x, \tau) = \overline{\varphi}_{ij}(x, \tau + \hbar \rho) \quad \tau < 0
\]

(3.7)

where the difference variable \( \tau = \tau_1 - \tau_2 \) is restricted to the domain \([-\hbar \beta, \hbar \beta] \). It is useful to extend the definition of \( \varphi_{ij} \) beyond this strip. Take \( \varphi_{ij} \) as periodic with

\[
\overline{\varphi}_{ij}(x, \tau) = \overline{\varphi}_{ij}(x, \tau + \hbar \rho)
\]

(3.8)

Then \( \varphi_{ij} \) can be developed in a Fourier series as:

\[
\overline{\varphi}_{ij}(x_i-x', \tau-\eta) = \int \frac{d^3 p}{(2\pi)^3} \frac{1}{\hbar^4} \sum \overline{\varphi}_{ij}(p, \omega_n) e^{ip(x_i-x')} e^{-\omega_n(\tau-\eta)}
\]

(3.9)
where
\[ \omega_n = \frac{i 2 \pi n}{\hbar}, \quad n=0,1,2,\ldots \]

and
\[ \Phi_{ij}(x-x_0, \omega_\nu) = \frac{1}{2i} \int_{-\hbar}^{\hbar} d(\tau-\tau_\nu) e^{\omega_\nu(\tau-\tau_\nu)} \Phi_{ij}(x-x_0, \tau-\tau_\nu) \]  
(3.10)

In precisely the same manner as for \( \Phi_{1j}^R \),
\[ \Phi_{ij}(p, \omega_n) = \int_{-\infty}^{\infty} d\omega' \frac{(\omega_n - \omega')^{-1}}{(e^{p\hbar \omega'} - 1)} A_{ij}(p, \omega') \quad n \geq 0 \]  
(3.11)

This spectral representation may be used to define an analytic
continuation into the entire upper half plane. Since \( \Phi_{1j}^R \)
and \( \Phi_{1j} \) agree on the infinite set of points \( \omega_n \), with a limit
point in their domain of analyticity, \( \Phi_{1j} \)'s analytic continuation
into the upper half plane coincides with \( \Phi_{1j}^R \)'s. Thus to determine
\( A_{ij} \) one calculates \( \Phi_{1j}(p, \omega_n) \), performs the trivial analytic
continuation, and takes the imaginary part.

B. Diagrammatic Perturbation Theory

As noted above \( \Phi_{1j} \) is essentially a one-particle
propagator, and may thus be calculated in a manner similar to
the Feynman-Dyson diagrammatic perturbation theory so successful in quantum electrodynamics. The rules for calculation of \( \Phi_{ij} \) will be given without proof since the procedure for their derivation for any given system is well-known.¹

Draw all topologically distinct, connected diagrams leading from an external photon absorption vertex and ending in an external photon emission vertex (represented respectively by a directed wavey line into the initial vertex and one out of the final vertex). One may regard the action of the first vertex as exciting an atom particle-hole pair, or equivalently as exciting an atom from the equilibrium configuration, resulting in a depopulation of the state from which the atom was excited. This particle-hole pair may then interact with the medium and each other until the system is returned to the equilibrium state by the photon emission. Hole lines are directed down and particle lines upward.

The system has been restricted to include two kinds of material particles and radiation. Atoms are represented by heavy solid lines, gas particles (perturbers) by thin solid lines, and transverse photons by wavey lines. Atoms, gas particles and photons each carry a momentum and frequency label, atoms labeled additionally by the state of internal excitation. Static interactions are represented by horizontal lines, dotted line for atom-gas interaction and dashed line for gas-gas interaction. (See fig. 1 for example graphs.)
Associated with each diagram in the perturbation expansion is a corresponding analytic expression which may be determined from the following rules:

1. Propagating lines
   (a) For each atom line write \( G_{\alpha'\alpha}^{(0)}(k,\omega_n) \)
       where
       \[
       G_{\alpha'\alpha}^{(0)} = \delta_{\alpha'\alpha} \left[ \pi \omega_n + \mu_{\alpha} - \epsilon_{\alpha'}(k) \right]^{-1} \tag{3.12}
       \]
   (b) For each gas particle line write \( G^{(0)}(p,\omega_m) \)
       where
       \[
       G^{(0)}(p,\omega_m) = \left[ \pi \omega_m + \nu_p - \epsilon(p) \right]^{-1} \tag{3.13}
       \]
   (c) For each photon line write \( D_{ij}^{(0)}(\omega_n) \)
       where
       \[
       D_{ij}^{(0)}(\omega_n) = \Delta_{ij} \langle \omega \rangle \left[ \omega_n - \hbar^* \omega^* \right]^{-1} \tag{3.14}
       \]

2. Interaction Lines
   (a) \( \langle k'\alpha',p' | V | k_1,k_2, p \rangle \) for atom-gas interaction. \( \tag{3.15} \)
   (b) \( \langle p_1'p_2' | V | p_1,p_2 \rangle \) for gas-gas interaction. \( \tag{3.16} \)
   (c) For each internal atom-radiation vertex write
       \[-(\hbar^*\hbar)^{1/2} \langle \alpha' | J_i | \alpha \rangle \] \( \tag{3.17} \).
3. Wave number and imaginary frequency conservation at every vertex require factors

\[ (2\pi)^3 \delta(\sum \mathbf{k}_{in} - \sum \mathbf{k}_{out}) \mathcal{G}_{\sum \omega_{in} \sum \omega_{out}} \]  

(3.18)

4. Integrate over all internal wave vectors and sum all imaginary frequencies according to

\[ \frac{1}{\rho} \sum_{\omega_n} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \]  

(3.19)

5. Affix an overall sign factor \((-1)^{n+F}\) where \(F = \) number of closed fermion loops, and \(n = \) the order of the graph. The order is determined by the number of interaction lines; a photon line is considered an interaction line here.

Finally, since perturbation theory is being used, it is necessary to specify the relevant smallness parameter. For the case of neutral particles interacting through short range forces, the dimensionless expansion parameter is \((nt)^\beta\), where \(n\) is the particle density and \(t\) is the gas-atom scattering amplitude. For a high temperature classical plasma the smallness parameter is proportional to \(e^2 n^{1/3}\). Further, the atom's level structure should be more or less left intact with interactions switched on; that is, shifts and splittings of the order of magnitude of the absorbed energy would be quite outside the domain of perturbation theory.
IV. IMPACT THEORY OF ABSORPTION LINE SHAPE

The prescription for the calculation of the total absorption rate was given in the last section in terms of rules for calculation of $\xi_{ij}(P, \omega)$ in a systematic perturbation theory expansion. Once $\xi_{ij}$ is known, from the spectral representation,

\[
(2i)^{-1}(\Phi_{ij}(P, \omega) - \Phi_{ij}^*(P, \omega)) = \text{Im} \frac{\Phi_{ij}(P, \omega)}{2} = \frac{i}{2} (1 - e^{-\beta \omega}) A_{ij}(P, \omega) \tag{4.1}
\]

Thus,

\[
\sigma_{ij}(P, \omega) = \frac{2\pi}{\omega} \left( \hbar c \right)^{\gamma} \langle \varepsilon_i \varepsilon_j \rangle \frac{\Phi_{ij}(P, \omega)}{2} = \frac{2\pi}{\omega} \left( \hbar c \right)^{\gamma} (1 - e^{-\beta \omega}) \text{Im} \frac{\Phi(P, \omega)}{2} \tag{4.2}
\]

where

\[
\frac{\Phi(P, \omega)}{2} = \varepsilon_i \varepsilon_j \Phi_{ij}(P, \omega).
\]

In this section an investigation of a particular theory of line broadening will be undertaken first, to gain familiarity with the general calculational procedure, and second, to obtain some insight into the complications special to line broadening.
In recent years a theory of line broadening has been developed and used with a certain measure of success. This work is essentially an amplification of an important paper by P. W. Anderson on microwave absorption. The fundamental assumption of this theory is that the perturbing effects of a foreign gas on an absorbing atom may be regarded as collisions non-overlapping in time, or if collisions occur simultaneously they are sufficiently weak as to justify first order perturbation theory in the single particle collisions. Such a theory has been quite useful in determining the perturbing effects of electrons, which to a certain extent do satisfy the "impact approximation" criteria. Here recoil effects will not be ignored and broadening due to radiative reaction will be discussed. Note that including recoil effects does not merely imply broadening due to Doppler shifting. The atom can recoil against perturber collisions as well as upon absorption of a photon. Finally, it will be apparent how one accounts for simple gas-gas correlation effects (shielding in a plasma, for example).

A. Radiation Broadening

Ignoring all perturber effects (see fig. la.), one obtains the usual result that only frequencies precisely equal to a level difference of the atom will be absorbed. If the effects of perturbation are included one might expect to relax this strict energy conservation with a particular level. However, if
contributions from so called self-energy graphs are included in some order of perturbation theory (for a complete discussion of self-energy functions see appendix III), the result will be a divergently large contribution to $\mathcal{Q}$ and hence the absorption rate. The origin of this anomalous result may be understood in the following manner: as far as radiation absorption is concerned, the atom may be regarded as a harmonic oscillator; further, the present perturbation theory has been developed in such a way that the external field acts for all time. Thus the atom responds to the field like an undamped oscillator which can realize arbitrarily large amplitudes. It is clear that if some damping were introduced the oscillation would always be amplitude limited.

The lowest order diagrams in radiative coupling contributing to $\mathcal{Q}$ are shown in Fig. 2. The "ladder" diagram 2c. is smaller than 2a. or 2c. by an extra power of the fine structure constant and may thus be ignored. Since the external field formally acts for an unlimited time, an infinite sequence of such diagrams must be summed. (See Fig. 3.) The double, heavy, solid lines represent the sum of the infinite sequence obtained by iterating Fig. 2a. Iterations of Fig. 2b. are not considered since they correspond to instability of the ground state against absorption from the incident beam or from the assumed thermal radiation. This approximate form for $\mathcal{Q}$ results in an absorption rate with the well-known Lorentz line shape, the width proportional to the rate of decay of the atom by radiative emission.
\[ \Phi(p, \omega) = (a) + (b) + (c) + \cdots = \text{Fig. 3} \]
B. Collisional Broadening

The result of including gas perturbing effects is shown in Fig. 4. The thick lines represent amplitudes in which all possible interactions with the gas or radiation are included. Contrary to the case of pure radiation damping, "ladder" diagrams must be retained (see Fig. 2c.), since they contribute terms to $\hat{\phi}$ of the same order of magnitude as the first graph of the sequence. Higher order graphs, examples of which are shown in Fig. 5., are outside the impact approximation. These graphs include collisions which are not separated in time and hence must be ignored. The utility of a diagram approach is clearly demonstrated here. Physical overlapping manifests itself directly as a topological overlapping in higher order diagrams. However, this intuitive picture is often obscured for systems of high density. That a given diagram may be analyzed directly in terms of the real collisions that the atom experiences in its excited lifetime is quite false.

1. Ladder Sequence and Integral Equations

(1) The special case. The contribution of Fig. 4a. to $\hat{\phi}$ is:

\[
\sum_{\alpha, \beta} \int \sum_{k, l, p} \sum_{\omega_n} G_{\alpha \alpha}^{k, l, p} \langle \beta | \hat{J} | \alpha' \rangle G_{\beta \beta}^{l, p, \omega_n} \langle \alpha' | \hat{J} | \beta' \rangle \times \langle \alpha | \hat{J} | \beta \rangle.
\]
\[ \Phi(p, \omega) = (a) + (b) + (c) + \ldots \]

**Fig. 4**

**Fig. 5**
Note that full propagation amplitudes are being used here, and, in general, these amplitudes are elements of a propagation matrix. In general, non-diagonal elements must be included in the above sums. In this section, however, assume:

1. \((\alpha, \alpha')\) are members of a single degenerate collection of states (neglecting overlapping lines),
2. damping does not connect different members within this degenerate collection, and
3. the same assumptions for the excited level.

(These restrictions will be removed after the frequency sum and analytic continuation are demonstrated for this simpler case).

Eq. (4.3) becomes:

\[
- \sum_{\alpha, \beta} \int d \mathbf{k} \phi_{\alpha \alpha} (\mathbf{k}, \omega_{\alpha}) \langle \mathbf{k} | \mathbf{v} | \mathbf{k} \rangle G_{\alpha \beta} (\mathbf{k}, \omega_{\alpha}, \omega_{\beta}) G_{\beta \beta} (\mathbf{k} + \mathbf{p}, \omega_{\alpha}, \omega_{\beta}) \langle \mathbf{k} | \mathbf{v} | \mathbf{k} + \mathbf{p} \rangle \]  (4.4)

where

\[
G_{\alpha \alpha} (\mathbf{k}, \omega_{\alpha}) = \left[ \omega_{\alpha} + \mu_{\alpha} - e_{\alpha} (\mathbf{k}) - \langle \mathbf{k} | \mathbf{v} (\mathbf{k}, \omega_{\alpha}) | \mathbf{k} \rangle \right]^{-1}
\]

with a similar expression for \(G_{\beta \beta}\).
For the details of the frequency sum and analytic continuation see Appendix I. Eq. (4.4) is:

\[
(e^{-i\beta\omega} - 1) \int \frac{d^3 k_1}{(2\pi)^3} \sum_{\alpha, \rho} \Pi_\alpha (k_1) (1 - \Pi_\rho (k_1 + P)) \langle \alpha | \hat{E} | \rho \rangle \\
\times \left[ \omega - \epsilon_\rho (k_1 + P) + \epsilon_\alpha (k_1) - \langle \rho | \Phi (k_1 + P) \Phi \rangle - \langle \alpha | \Phi (k_1) \Phi \rangle \right]
\]

(4.5)

where \( \Pi_\gamma (k_1) \) is the equilibrium distribution function for the absorbing atom,

\[
\Pi_\gamma (k_1) = \left[ e^{\left( \mu_\gamma - \epsilon_\gamma (k_1) \right)} + 1 \right]^{-1}
\]

(4.6)

and \( \langle \gamma | \Phi^\pm (k) | \gamma \rangle \) are the self-energy functions of the atom in a state of c.m. momentum \( k \) and internal state \( \gamma \).

To continue, it is convenient to define

\[
\sum_{\rho, \alpha} | (K_1, \omega_1, k_1, + P, \omega_1, + \omega_n) \rangle \langle \rho, K_2, \omega_n, + \omega_n | = \int \frac{d^3 k_2}{(2\pi)^3} \int \frac{d^3 k_3}{(2\pi)^3} \sum_{\omega_n} G_{\alpha, \rho} (k_1, \omega_n) \times \\
G_{\alpha', \rho} (k_2 + P, \omega_n, + \omega_n) \langle \beta, K_2, - P, - \omega_n, \omega_n, + \omega_n \rangle \times \\
\langle \alpha', K_2, - P, - \omega_n | V | \alpha, k_1, + P, \rangle \sum_{\omega_m} G^{(o)} (\omega_n, + \omega_m, + \omega_n, \omega_m, + \omega_n) \times \\
G^{(o)} (\omega_m, + \omega_m | P, \rangle)
\]

(4.7)
and

\[ \Lambda^{(o)}_{\alpha'\beta'\gamma'\delta'} = \delta_{\alpha\alpha'} \delta_{\beta\beta'} \delta_{\gamma\gamma'} \delta_{\delta\delta'} \]  \hspace{1cm} (4.8)

Then the first two diagrams of Fig. 4 are:

\[ \sum_{\alpha', \beta', \gamma', \delta'} \int \frac{d^4k}{(2\pi)^4} \sum_{\omega_n} \bra{\alpha' k} \Lambda^{(o)}_{\alpha'\beta'\gamma'\delta'} \ket{\beta' k} \left[ \Lambda^{(o)}_{\beta'\gamma'\delta'\epsilon'} + \Lambda^{(o)}_{\beta'\gamma'\delta'\epsilon'} \right] \times 
\]

\[ G_{\alpha\epsilon} (k, \omega_n) G_{\beta'\epsilon'} (k + p, \omega_n + \omega_n) \]  \hspace{1cm} (4.9)

\( \Lambda^{(o)} \) and \( \Lambda^{(1)} \) may thus be regarded as vertex functions. For an arbitrary member of Fig. 4 consider

\[ \Lambda^{(o)}_{\alpha'\beta'\gamma'\delta'} (\omega_n, k, \omega_n + \omega_n, k + p) \]

as shown in Fig. 6. Then

\[ \Phi (p, \omega) = \sum_{\alpha', \beta', \gamma', \delta'} \int \frac{d^4k}{(2\pi)^4} \sum_{\omega_n} \bra{\alpha' k} \Lambda^{(o)}_{\alpha'\beta'\gamma'\delta'} (\omega_n, k, \omega_n + \omega_n, k + p) \times
\]

\[ \bra{\beta' \epsilon'} G_{\alpha\epsilon} (k, \omega_n) G_{\beta'\epsilon'} (k + p, \omega_n + \omega_n) \]  \hspace{1cm} (4.10)

where
and, for convenience, momentum dependence has been suppressed. From the form of \( \Lambda^{(s)} \) it is obvious that it may be expressed in terms of \( \Lambda^{(s-1)} \) as in Fig. 7a. But this result implies an integral equation for \( \Lambda \) itself as schematically represented in Fig. 7b. Thus,

\[
\begin{align*}
\Lambda_{\alpha\beta}(\omega_n, \omega_n + \omega_n) = & \delta_{\alpha_0, \beta_0} \\
= & \sum_{\alpha_0, \beta_0} \int \frac{d^3 k}{(2\pi)^3} \frac{1}{\omega_{k_0}} \sum_{\omega_{k_0}} G_{\alpha_0 \beta_0 \alpha_0} \left( k_0, \omega_{k_0} \right) G_{\beta_0 \alpha_0 \beta_0} \left( k_0 + P, \omega_{k_0} + \omega_n \right) \\
& \times \int \frac{d^3 p}{(2\pi)^3} \left( \alpha_0, k_0, p, \frac{3}{2} V \right) \left( \alpha_0, k_0, P, \frac{3}{2} V \right) \left( \beta_0, k_0, P, \frac{3}{2} V \right) \left( \beta_0, k_0, P, \frac{3}{2} V \right) \\
& \times \frac{1}{\omega_{k_0}} \sum_{\omega_{k_0}} G^{(\omega)}(\omega_n, \omega_n + \omega_n, \omega_n + \omega_n) G^{(\omega)}(\omega_n, \omega_n, \omega_n) \Lambda_{\alpha_0 \beta_0 \alpha_0 \beta_0}(\omega_{k_0}, \omega_{k_0} + \omega_n)
\end{align*}
\]

The frequency summation and analytic continuation procedure require some special care since \( \Lambda^{(\omega_n, \omega_n + \omega_n)} \), when analytically continued, has several branches. (See Appendix I for details.) Upon taking the low-density limit for the absorbing atoms, \( \Lambda^{(s+1)} \) satisfies
\[ \Lambda^{(s)}(\omega_{n_1}, k_1 \mid \omega_{n_1} + \omega_n, k_1 + p) = \alpha_1 \beta_1 \mid \alpha' \beta' \]

**Fig. 6**

\[ \Lambda^{(s)}(\omega_{n_1} \mid \omega_{n_1} + \omega_n) = \alpha_1 \beta_1 \mid \alpha' \beta' \]

\[ \Lambda = \Lambda^{(0)} + \]

**Fig. 7**
\[
\chi_{\alpha' \beta'}(k, l, p) = \delta_{\alpha \alpha'} \delta_{\beta \beta'}
\]

\[
= - \sum \int \frac{d^3 k_2}{(2\pi)^3} \int \frac{d^3 p}{(2\pi)^3} \eta(p) \left(1 - \eta(p, q)ight) \gamma \left(\delta \left(\varepsilon_{\alpha} - \varepsilon_{\alpha'} + \varepsilon(p) - \varepsilon(p, q)\right) \langle \lambda_{\alpha} k_{\alpha}, p, q \mid \lambda \lambda_{\alpha} k_{\alpha}, z_{\alpha'} \rangle \right) \quad (4.13)
\]

\[
\times \chi_{\alpha' \beta'}(k, l, p) \langle \lambda \lambda_{\alpha} k_{\alpha} + p, z \mid \psi \rangle \langle \lambda_{\alpha} k_{\alpha} + p, p, q \rangle
\]

\[
\times \left[ \omega - (\varepsilon_{\alpha} k_{\alpha} + p) - \varepsilon_{\alpha'} k_{\alpha'} - (\varepsilon_{\beta} \bar{\Phi} k_{\beta} + p) - (\varepsilon_{\beta'} \bar{\Phi} k_{\beta'}) - (\varepsilon_{\alpha} \bar{\Phi} k_{\alpha} + \varepsilon_{\alpha'} \bar{\Phi} k_{\alpha'}) \right]^{-1}
\]

where the \( \pm \) designation corresponds to a particular branch of the analytically continued \( \Lambda \). It is important to note that the presence of \( \delta \) energy appears here since only completed, non-overlapping collisions are represented. \( \langle \alpha', \beta' \rangle \) act merely as free indices in the above equation. This simplifying feature will be lost when the more general case is considered in which the propagation matrix has off-diagonal elements. Finally, the self-energy functions are dependent on frequency in general.
it has been assumed that they are sufficiently slowly varying that
they may be evaluated as:

\[ \hbar \omega = \varepsilon_{\rho}(k_x + P) - \varepsilon_{\alpha}(k_x) \]  \hspace{1cm} (4.14)

Thus, one is assured that only completed collisions contribute
to the line shape since only on-energy-shell scattering amplitudes
are used.

It is possible to put the expression for the total absorption
rate in a more compact form by defining the amplitude:

\[ \mathcal{M}_{\alpha \beta | \alpha' \beta'}(P, \omega) = \mathcal{M}_{\alpha \rho | \alpha' \rho'}(k_x, k_x + P) \]

\[ \times \left[ \omega - (\varepsilon_{\rho}(k_x + P) - \varepsilon_{\alpha}(k_x)) - (\langle \rho | \bar{\Phi}(k_x + P) | \rho \rangle - \langle \omega | \bar{\Phi}(k_x) | \omega \rangle) \right] \]  \hspace{1cm} (4.15)

Then,

\[ \bar{\Phi}(P, \omega) = (e^{-\rho \hbar \omega}) \sum_{\alpha \beta} \int_{\mathbb{C}^3(k_x)} \mathcal{M}_{\alpha \beta | \alpha' \beta'}(P, \omega) \langle \rho | \bar{\Phi}(k_x) | \omega \rangle \]

\[ \times \langle \alpha | \bar{J} \cdot \hat{E} | \beta \rangle \mathcal{M}_{\alpha \beta | \alpha' \beta'}(P, \omega) \langle \rho' | \bar{J} \cdot \hat{E} | \omega \rangle \]  \hspace{1cm} (4.16)

where \( \mathcal{M}_{\alpha \beta | \alpha' \beta'} \) satisfies the set of integral equations:
The "collision-integral" kernel $K$ is:

$$K^{K_1, K_2} (P) = \frac{i}{8\pi} \int \frac{d^3 p_1}{(2\pi)^3} \frac{d^3 p_2}{(2\pi)^3} \frac{d^3 k_1}{(2\pi)^3} \frac{d^3 k_2}{(2\pi)^3} \langle \rho | \Phi_1 (P, p_1) \Phi_2 (P, p_2) \rangle (\alpha_{K_1} \alpha_{K_2})$$

where

$$\delta^{(3)} (k, p - k_1 - p_2) \delta (\epsilon_k - \epsilon_{k_1} - \epsilon_{p_1} - \epsilon_{p_2})$$

$K$ cannot be interpreted as resulting from collisions of gas particles with the atom in either the upper or lower levels. Rather, it represents a coherent interference effect due to scattering from both of them. The physical meaning of Eqs. (4.16) and (4.17) will be discussed after the general case including overlapping lines and degeneracy is considered.
(2) The general case. As was noted above, although $\Lambda_{\alpha\beta}^{++}$ and $\Lambda_{\alpha\beta}^{+-}$ are objects labeled by four internal states, two of these labels are free parameters which may be ignored in the solution of Eq. (4.17). The more general situation results in essentially the same equations; however, all four indices are involved in a non-trivial manner.

In the previous section it was assumed that the propagation matrix could be approximated by its diagonal elements. Further, all levels were assumed well-separated; i.e., the collisional interaction did not result in overlapping of lines. When the levels are so strongly coupled that their individuality is washed out, it is necessary to solve a new eigenvalue problem for these states. Thus in the course of obtaining the final result, a new Schrodinger equation for the atom must be introduced, where the self-energy operator plays the role of a pseudopotential. Then the algebraic manipulations of the analytic continuation closely parallel the special case.

To return to original basis for the internal states of the atom, a dyad vector space was used. This space is analogous to the vector space in which the quantum Liouville operator acts. It is important to realize, however, that the Liouville operator acts on full states of the system rather than the internal states of the absorbing atom. U. Fano has employed such a formalism to derive a theory of collision broadening. Fano formally exhibits a cluster expansion for the line shape, but the generality of the
result is deceptive since the Liouville operator method is necessarily restricted to the case of non-interacting statistics and thus is valid only to first order in the density of the perturbing gas. The Green's function approach does not suffer from this deficiency.

The dyad vector space is an ordered pair of internal states of an atom. Given an operator \( Q \), acting in the space spanned by the internal states of an atom, one may construct two different operators acting in the dyad space. For a given \( \alpha \), define

\[
\langle \alpha | Q L | \alpha' \rangle = \delta_{\alpha \alpha'} \langle \alpha | Q | \alpha' \rangle \quad (4.19a)
\]

\[
\langle \alpha | Q R | \alpha' \rangle = \delta_{\alpha \alpha'} \langle \beta | Q | \beta' \rangle \quad (4.19b)
\]

 Closure is expressed by:

\[
\sum_{\alpha \beta} |\alpha \beta\rangle \langle \alpha \beta| = \mathbb{I} \quad (4.20)
\]

The \( \alpha, \alpha', \ldots \), denote a collection of states with approximately the same energy and strongly coupled by the effects of collisions. The \( \beta, \beta', \ldots \), are similarly chosen but with energies exceeding the \( \alpha \) group by approximately the energy of the absorbed radiation.

This formal device enables one to transcribe the results of the special case to the general situation. Now, however, \( M_{\alpha \beta}^{\kappa_1} \alpha' \beta', (\mathcal{P}, \omega) \) is to be regarded as an element of the matrix operator \( M \).
in the dyad space. $M^1(E,\omega)$ satisfies the matrix-integral equation:

$$\left[\omega - (H_R^0(K,F) - H_L^0(k)) - \langle \bar{\phi}^+(k,F) \rangle_{R^0} - \langle \bar{\phi}^+(k,F) \rangle_{L^0}\right] M^1(E,\omega)$$

$$= I + \int \frac{d^3K_k}{(2\pi)^3} K^{K,K_x}(E,\omega) M^1(E,\omega)$$

(4.21)

The kernel for the collision operator is defined by:

$$K^{K,K_x}(E,\omega) = i \int \frac{d^3R}{(2\pi)^3} \frac{d^3P_x}{(2\pi)^3} n(R) (1 - n(P_x))$$

$$\times (2\pi)^3 \delta(K_x - K_x - P_x - P_x) \delta(E_x, E_x) \delta(E_x - E_x - E_x - E_x)$$

$$\times \langle \phi_1^- \rangle \langle T^+(k_x, P_x, P_x, F, F) \rangle \langle T^+(k_x, P_x, P_x, F, F) \rangle R^{K_x K_x}$$

$H^0_O^{(R,L)}(k)$ is a dyad-space operator obtained from the free-atom Hamiltonian. Similarly, $\phi^{(R,L)}$ are the corresponding self-energy operators. $T^\pm$ is the two-particle scattering matrix (see appendix I).

2. Discussion

The integral-matrix equation satisfied by $M$ reduces to a matrix equation in the dyad vector space when recoil may be ignored. Then,
If the effects of Doppler shifting and radiative reaction are ignored, this result is precisely the Anderson-Baranger theory of line broadening. However, if the mass ratio of perturbers to absorbers is not small, recoil effects must be considered. Then the problem is essentially a marriage of a D.C. conductivity calculation and what is typically regarded as a line broadening calculation. That is, momentum dissipation as well as internal-state excitation are present. For example, if one is interested in the special case of self-broadening (absorbing and perturbing atoms are identical), the recoil complication must be understood.

The role of the impact approximation is quite clear in the above treatment. If the self-energy functions were not smooth functions of frequency, the impact criterion would not be satisfied, and the line shape would not be determined simply by completed collisions. Indeed, one may investigate the limits of the impact regime by considering the self-energy function itself. For example, it is to be expected that the contribution of ion broadening to the line shape is characterized by a self-energy function which is a sensitive function of \( \omega \).

Finally, the effects of gas-gas correlations may be
included in a systematic fashion. In a plasma the coulomb interaction is shielded through charged particle correlations. This effect is included by replacing the collision interaction $V(q)$ by the well-known screened dynamic interaction $V(q, \omega)$.
V. PARTIAL RATES AND GAS COLLISION PROCESSES

A. Scattering and Gas Reactions

In the last section the total absorption rate in the impact approximation was calculated in a manner which made no explicit reference to the various modes of decay open to the excitation. An alternative interpretation of the total absorption rate is suggested by scattering theory. One may regard the total rate as equal to the sum of partial rates for certain scattering processes, the sum extending over all channels open to the initial radiation beam and the thermal target. Thus given the rate for the occurrence of certain processes initiated by the incident radiation, one may construct the total rate and hence the line shape. Conversely, one might be able to interpret the detailed development of the line in terms of well-defined processes.

In scattering theory a scattering event is defined if the initial and final asymptotic conditions of the system are specified. As an example consider the stripping reaction of fig. 8. Associated with this event is a probability amplitude, which in principle is known given the Hamiltonian of the system.

Intuitively the scattering picture is immediately applicable to reactions initiated by a particle incident on a gas. As examples one may consider the competing processes of quenching of an atom excited by resonance radiation and fluorescence (Fig. 9a., 9b.). However, the analytic expression of this picture is not immediately apparent.
Fig. 8

Fig. 9

(a)  (b)
since, generally speaking, the particles are never asymptotically free. That is, the particles in the gas which compose the initial and final state are in interaction with the other particles of the gas. Clearly this difficulty must be of a purely formal nature; the intuitive scattering picture is obviously a good one, at least for low density systems.

The root of the difficulty stems from the fact that the above scattering picture is itself based on a perturbation-like construction, where, for example, (as in Figs. 9a, 9b.) the gas particles are representable as a statistical ensemble of free beams. Thus, to impart analytical meaning to the intuitive picture one must make appeal to perturbation theory from the very outset. To be acceptable such a perturbation theory should satisfy certain minimal criteria:

1. the sum of the partial rates for all processes yields the total rate in that particular order of perturbation theory,

2. the asymptotic nature of the scattering event results in initial and final states which may be defined unambiguously, and

3. these asymptotic initial and final states are connected by overall momentum and energy conservation.
B. Reduced Diagrams and Diagram Cutting

To proceed it is useful to consider a particular example in the calculation of the total rate. Figures 2a., b., c., represent the lowest order diagrams in radiative coupling. If one explicitly calculates the contribution to the discontinuity of $\mathcal{J}$ across the real axis (equivalent to $\text{Im} \mathcal{J}$), it is possible to rearrange the result in such a way as to exhibit a certain natural grouping of the terms. In particular, included is a collection of terms which may be symbolically represented as in Fig. 10a. These "open diagrams" are calculated according to the "closed diagram" rules for the amplitude $\mathcal{J}$. The probability obtained from the amplitude represented by Fig. 10a is multiplied by a four-dimensional $\delta$-function corresponding to momentum and energy conservation for the scattering of light from an atom and some obvious statistical factors. The special appeal of this result is understood upon comparing with Fig. 10b., the usual Feynman diagrams whose calculation yields the well-known Kramers-Heisenberg light dispersion formula.

If it is possible to generalize from this simple example, one might propose to calculate the partial rate for a given process by writing down all the diagrams with the same initial and final state (all coherent amplitudes), take the complex-conjugate-square of the sum of these amplitudes, and affix the appropriate energy-momentum conservation factor. Indeed, this "open diagram" procedure has been conjectured in a study of wave propagation in plasmas.
The method enjoys significant calculational advantage over the "closed diagram" approach and, as well, enhances one's understanding of the various microscopic processes involved.

Unfortunately certain ambiguities arise when reactive processes are important necessitating infinite graph summations. In particular, it is not always possible to put the various contributions to the discontinuity of $\phi$ in a unitary-like sum without running the risk of overcounting certain diagrams. Thus, the operation of "diagram cutting," i.e., deriving an open diagram expansion from the corresponding closed diagram expansion, does not always commute with infinite graph summation. The work of DuBois et al does not suffer from this difficulty since reactive effects are unimportant in their calculations.

A less ambitious approach can be followed which does not suffer from the above ambiguity, and for which an analytical proof may be constructed. To motivate this alternative procedure, it is convenient to return to the light scattering example. The scattering rate was proportional to

$$\| A + B \|^2 = AA^* + BB^* + A^*B + BB^*$$  \hspace{1cm} (5.1)

(For a pictorial representation see Fig. 10c.) A given diagram contributing to the total absorption rate is cut into two pieces, each one including an external photon vertex. The two pieces have amplitudes associated with them which are calculated according to
the usual diagram rules. (Note that all possible cuts are to be taken. In the present example, the two cuts corresponding to $AB^*$ and $B^*A$ are derived from the same closed diagram.) This procedure for calculating the spectral function $A(E,\omega)$ is essentially the "reduced" diagram scheme of Landau and Cutkosky, used to analyze the analytic properties of the Feynman diagrams of relativistic field theories. This technique has also been applied to conductivity calculations at both zero and finite temperature. J. S. Langer has proved the generalization of the method to finite temperature for a normal interacting Fermi gas. In Appendix II a simplified but heuristic derivation is given applicable to the present system.
\[ \frac{1}{f} \left( \frac{1}{f} + \frac{1}{f} \right) \]

(a)

\[ \frac{1}{f} \left( \frac{1}{f} + \frac{1}{f} \right) \]

(b)

(c)

Fig. 10
VI. RESONANCE FLUORESCENCE AND QUENCHING

A. Reduced Diagram Expansion

The two radiation absorption processes considered in the last section, fluorescence and quenching, may be investigated in detail through the use of the reduced diagram expansion. Fluorescence here is to be regarded as photon scattering out of the initial beam, whereas, quenching corresponds to actual heating of the gas without photon emission. Energy is communicated to the gas through a diabatic collision between the atom and a gas particle. Such a collision may also be accompanied by radiative emission, and this possibility appears naturally in the appropriate reduced diagram expansion. The emission line for such a process will contribute predominately to the "wing" spectrum.

For ease of interpretation, it is useful to consider only those cases for which broadening in the lower state is unimportant. This situation is often realized in practice. The atom is more tightly bound and compact and thus less readily polarized in its lower state than in the upper level. The Lyman series of hydrogen may be approximated in this manner. Some lines of helium may similarly be treated. The total absorption rate is then proportional to the discontinuity of the amplitude of Fig. 11. This fully renormalized amplitude is expanded in gas collisions and the propagator renormalized to radiative corrections as shown in Fig. 12.
Consider the contribution to the discontinuity of the total amplitude from Fig. 11a. In particular, consider all possible reduced diagrams which include a single photon line. (See Fig. 13a.) But these diagrams are equivalently written as in Fig. 13b., and hence may be regarded as photon absorption followed by photon emission; i.e., photon scattering. The reduced diagrams in which the atom remains in an excited state need not be considered since the atom will always finally be de-excited. The diagrams shown in Fig. 11b., 11c., etc. contribute further reduced graphs in which a single photon line and an atom hole-particle pair is cut.

The excited atom may be de-excited by diabatic collisions as well as by photon emission. Here diabatic is taken to mean a transition of the atom from an excited state to the ground state of the atom—-the line is quenched. The diagram of Fig. 11c. yields the lowest order contribution to the absorption rate in which a gas particle may be excited through collision with the excited atom. Coherent with this term are all the higher order collision corrections with reduced diagrams in which an unexcited atom particle and hole line appear simultaneously with a gas-particle hole and particle line. (See Fig. 14b.)

The cut shown in Fig. 14a. may be regarded as contributing to the fluorescent rate of the atom. When collisional broadening is important additional processes, although incoherent with that of Fig. 14a., must be analyzed to properly assess the emission
Fig. 13
Fig. 14
line or the total fluorescent yield. As examples, note the reduced graphs of Fig. 14c. In general, write:

\[ \Gamma_T = \Gamma_Q + \Gamma_F, \quad \Gamma_F = \sum_{j=0}^{\infty} \Gamma_F^{(j)} \]  

(6.1)

where \( \Gamma_Q \) is the quenching rate, corresponding to de-excitation of the atom purely through diabatic collision with a gas particle. This quantity is determined by the reduced graph of Fig. 14b. The second term includes all possible processes in which a final photon is present—the emission line. \( \Gamma_F^{(0)} \) is precisely the partial rate represented by the cut of Fig. 14a. On physical grounds, separating out \( \Gamma_F^{(0)} \) is in a certain sense artificial. However, in the event that collisions may be ignored, this quantity is just the scattering rate of resonance radiation and hence useful as a comparison.

Consider the cut of Fig. 14a, or 15 in detail. If it is possible to write it in a unitary-like-sum form, it is natural to identify \( \Gamma_F^{(0)} \) as a partial rate, contributing to the fluorescent yield. Since the lines retained in the reduced diagram are free propagators, it follows that:

\[ \hbar \omega_{m} \rightarrow e_{x}^{\epsilon}(k) - \mu_e, \quad \hbar \omega_{m} \rightarrow \hbar \omega \]  

(6.2)

\[ \hbar \omega_{n} \rightarrow e_{x}^{\epsilon}(k') - \mu_e, \quad \hbar \omega_{m} \rightarrow \hbar \omega' \]  

(6.3)
As shown in Appendix II, the contribution to the total absorption rate from a particular reduced diagram is a product of five factors: a statistical factor $S$, a factor containing a product of the spectral functions of the lines of the reduced graph $Z$, two vertex amplitudes $A_1, A_2$, and an energy-momentum $8$-function. The amplitude factor

$$A_2(\omega - i\epsilon)A_1(\omega + i\epsilon) \sum_{\lambda \rho \rho'} \left[ \langle \lambda J \bar{\lambda} \rangle \langle \rho \rho' \rangle \right] G_{\lambda \rho \rho'} (\epsilon_{\lambda} (k) + \pi \omega - i\gamma, \pi \omega + i\gamma)$$

$$\times \frac{(4\pi \hbar)^{\frac{L}{2}}}{\sqrt{2\pi \omega'}} \left( \beta \bar{\beta} \right) \sum_{\beta \beta'} \left[ \langle \beta' J \bar{\beta'} \rangle \langle \beta \beta' \rangle \right] \frac{(4\pi \hbar)^{\frac{L}{2}}}{\sqrt{2\pi \omega'}}$$

$$\times \left\{ G_{\lambda \rho \rho'} (\epsilon_{\lambda} (k) + \pi \omega + i\gamma, \pi \omega + i\gamma) \right\}$$

(6.4)

Now,

$$A_2(\omega - i\epsilon) = A_1^*(\omega + i\epsilon)$$

(6.5)

Thus,
Similarly, the quenching rate is proportional to

\[ \Gamma^\prime = \sum_{\alpha'\alpha} \int \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \frac{d^3p}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \rho_{\alpha'}(k) \rho_{\alpha}(p) (1 - \rho_{\alpha'}(k')) \]

\[ \times \left( 1 - \rho_{\alpha'}(p') \right) \theta(k + P + p - p' - k') \delta\left( E_{\alpha}(k) + \hbar \omega + \epsilon(p) - E_{\alpha'}(k') - \epsilon(p') \right) \]

\[ \times \left| \sum_{\beta'\beta} \langle \beta' | T^{\prime} | \beta \rangle \rho_{\alpha}(p, k + P) \rho_{\beta'}(p, k') \right|^2 \]

(6.7)

These are schematically represented by Figs. 16a., 16b., respectively.

Here the Born approximation for the quenching collision has been replaced by the full Born series (see Appendix I). These expressions will be discussed after the cuts of Fig. 14c. are considered.

By analogy with the cuts of Figs. 14a. and 14b., the contributions of the cuts of Figs. 14c. (i), (ii), (iii), and (iv), may be represented by Figs. 16c. (i), (ii), (iii), and (iv), respectively.
respectively. Indeed, if these processes have coherent final states, then their total contribution may be written as the complex square of two coherent probability amplitudes as shown in Fig. 16d.

Figure 16d. has a clear interpretation. The "final" state includes a photon of possibly different energy from the incident photon and a gas particle which through energy conservation makes up for the difference in energy. If the atom may actually be regarded as in an excited state prior to the photon emission (for example, if the atom is stimulated by an excitation line continuous over the absorption line of the atom,) then the emitted radiation contributes to the emission line of the atom. This emission rate might be important in opacity calculations where the wing spectrum is needed. Alternatively, if the excitation and de-excitation must be regarded as a coherent process, then study of the emitted radiation outside the core of the emission line could be useful in investigating aspects of the diabatic gas collision from levels other than the resonantly excited one. Detailed analysis of these rates will not be considered here. \( \Gamma_Q \) and \( \Gamma_F^{(0)} \) as defined by Eqs. (6.7) and (6.6) may be simplified considerably in certain cases. It is useful to see to what extent they may be related to experimentally determined quantities. Only \( \Gamma_F^{(0)} \) will be discussed in detail since similar arguments are applicable to \( \Gamma_Q \).
B. Approximate Expressions for $\Gamma_F(0)$ and $\Gamma_Q$

$\Gamma_F(0)$ may be written

$$\Gamma_F = \int \frac{d^3k}{(2\pi)^3} \Delta \langle \phi \rangle F(k, P)$$

(6.8)

where

$$F_x(k, P) = \sum_{m_x, m'_x} \int \frac{d^3k'}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{2\pi}{\hbar} \delta \left( \varepsilon_a(k') + \hbar \omega' - \varepsilon_a(k) - \hbar \omega \right)

\times \sum_{\vec{E}} \sum_{\vec{E}'} \left| \sum_{\vec{E}''} \langle \vec{E}'' \vec{E} \vec{E}' \rangle \right|^2

\times \frac{(4\pi \hbar^2)^{1/2}}{\sqrt{2\hbar^2 \omega}} G_{\mu'} (\varepsilon_a(k') + \hbar \omega', k + P) \langle \rho | V_r | \rho \rangle \langle \rho | V_r | \rho \rangle$$

(6.9)

Here the initial photon polarization is averaged, and the radiation coupling matrix elements are written in terms of rotationally invariant operators. Also, the limit of Maxwell-Boltzmann statistics is taken.

As discussed in Appendix IV., for a number of situations

$$G_{\rho', \rho''} = G_{\rho', \rho''} \delta_{\rho', \rho''} \delta_{\rho', \rho''} G^{(\rho')}_{\rho'}$$

(6.10)
In Eq. (6.9) the states $\alpha$, $\alpha'$ have been assumed to correspond to a single level characterized by the angular momentum $J_\alpha$. Thus in the sum over $\beta$, $\beta'$ only terms labeled by $J_\alpha + 1$, $J_\alpha$ are allowed for dipole radiation. Further, if levels with these angular momentum are sufficiently separated in energy as to be considered non-overlapping, then the sum in the brackets reduces to a single sum over the spin projection $M_\beta$. Equation (6.9) becomes:

$$E_\alpha(k, P) = \left| G_{\alpha}^{(T)} \left( \epsilon_{\alpha}(k) + i\omega^+ c + P \right) \right|^2$$

$$\times \int \frac{p' d \rho' \delta(p-p')}{\hbar^2} \sum_{j \lambda} \sum_{\lambda} \left| \sum_{\lambda} \langle p' \lambda \lambda' | V_{\rho} \rangle \langle \rho | \lambda \rangle \tilde{e}_{\lambda} \right|^2 (6.11)$$

The second integral in Eq. (6.11) may be written:

$$\sum_{\lambda \lambda'} \left( \langle \rho | V_{\rho} \lambda \lambda' (P) V_{\rho} | \lambda \rangle \langle \lambda | V_{\rho} \lambda \lambda' (P) V_{\rho} | \lambda \rangle \right) (6.12)$$

where

$$\Lambda_\alpha (P) = \int \frac{d \rho \rho^*}{\hbar^2} \Lambda_\alpha (P), (6.13)$$

and
\[ \Lambda_{\alpha}(p) = \sum_{M_{\alpha}, \xi_{\alpha}} |P \xi_{\alpha} \rangle \langle P \xi_{\alpha}| \] (6.14)

\( \Lambda_{\alpha}(p) \) is clearly a rotationally invariant operator. Thus, the first matrix element vanishes for \( M_B = M_B' \), and in Eq. (6.11) the sum over \( M_B \) may be removed from the squared quantity.

Finally, the lowest order contribution to the total absorption rate from resonant photon scattering is (see Eq. 2.17):

\[ \sigma^{(0)}(p) = n_{\omega} \frac{1}{\Delta \omega} \left( \frac{\mu(p)}{\mu(0)} \right) \sum_{p} \langle \xi_{\alpha} \rangle \langle \xi_{\alpha} \rangle \left( \left| G^{(0)} \langle \xi_{\alpha} | \xi_{\alpha} \rangle + \hbar \omega | k + p \rangle \right|^2 \right) \] (6.15)

where

\[ L_{\alpha}(p) = \sum_{M_{\alpha}} \frac{P}{2 \pi} \int d^3 \rho \sum_{\xi_{\alpha}} \left| \langle \xi_{\alpha} | \rho \rangle \right|^2 \] (6.16)

the transition rate for photon emission. The brackets denote a thermal average over c.m. wave number of atom. For the case in which the atom is isolated, Eq. (6.15) reduces to the well-known result for scattering of resonance radiation. More generally, Eq. (6.15) includes the effects of collisional broadening and Doppler shifting. Further simplifications of Eq. (6.15) will be discussed later.
For the quenching rate:

\[ \Gamma_Q = \int \frac{d^3k}{(2\pi)^3} \frac{d^3p}{(2\pi)^3} Q_\alpha(k, p, P) n_\alpha(k) n(p), \]  

(6.17)

where

\[ Q_\alpha(k, p, P) = \sum_{m_n, m_{n'}} \int \frac{d^3k'}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} 2\pi n \delta \left( E_\alpha(k) + \hbar \omega + \varepsilon(p) - E_\alpha(k') - \varepsilon(p') \right) \]

\[ \times (2\pi)^3 \delta \left( k + P + p - k' - p' \right) \]

\[ \frac{1}{2} \sum_{\tilde{\epsilon}_\alpha} \left| \sum_{\tilde{\epsilon}_\alpha'} \left\langle \delta \left( \tilde{\epsilon}_\alpha' \right) \right| T^* \left( \delta \left( \tilde{\epsilon}_\alpha \right) + \hbar \omega + \varepsilon(p) \right) |\tilde{\epsilon}_\alpha \rangle \right|^2 \]

(6.18)

Similar arguments to those used in simplifying \( F_\alpha \) reduce \( Q_\alpha \) to:

\[ Q_\alpha = \int \frac{d^3k}{(2\pi)^3} \frac{d^3p}{(2\pi)^3} 2\pi n \delta \left( E_\alpha(k) + \hbar \omega + \varepsilon(p) - E_\alpha(k') - \varepsilon(p') \right) \]

\[ \times (2\pi)^3 \delta \left( k + P + p - k' - p' \right) \sum_{m_n, m_{n'}} \frac{1}{2} \sum_{\tilde{\epsilon}_\alpha'} \left| \left\langle \tilde{\epsilon}_\alpha' \right| T^* \left( \delta \left( \tilde{\epsilon}_\alpha \right) + \hbar \omega \right) + \varepsilon(p) \right| \left\langle \tilde{\epsilon}_\alpha + P | p, \hat{P}, \alpha \right\rangle \right|^2 \]

(6.19)

\[ \times \left| \left\langle \beta | \hat{V}_h | P, \hat{P}, \alpha \right\rangle \right|^2. \]
Note that the collisional de-excitation probability is not directly related to the de-excitation cross-section from an excited atomic state since it is evaluated at the initial and not intermediate energy of the atom-particle system. Similarly, the energy conservation connects the final state with the initial state—the nature of the excitation line is "remembered."

It is convenient to relate the quenching rate to an associated beam experiment in which an atom is excited by impact with subsequent photon emission. Indeed, it is the excitation cross-sections which are determined experimentally.

By space and time inversion symmetry,

\[ |\langle k' M_\alpha J_{\alpha} \beta | T^* (\xi_{\alpha}(k) + \hbar \omega + \epsilon(p)) | (p+K) m_\rho J_\rho \beta \rangle|^2 = \]

\[ |\langle (p+K) - m_\rho J_\rho \beta | T^* (\xi_{\alpha}(k) + \hbar \omega + \epsilon(p)) | k' - m_\alpha J_{\alpha} \beta \rangle|^2 \]

Under the sums over spin projections set \(- M_\beta \rightarrow M_\beta^\prime\) and \(- M_\alpha \rightarrow M_\alpha^\prime\).

Similarly,

\[ \sum_{m_\alpha} |\langle J_\rho - \omega \rho | \hat{J} \cdot \hat{J} \cdot \xi_{\alpha} m_\alpha \rangle|^2 = \sum_{m_\alpha} |\langle J_\rho m_\rho | \hat{J} \cdot \hat{J} \cdot \xi_{\alpha} m_\alpha \rangle|^2 \]  \hspace{1cm} (6.21)

In the expression for \( \Gamma_Q \) set \( P + k \rightarrow k \). With this change,

\[ \delta\text{-energy} \rightarrow \delta(\xi_{\alpha}(k') + \epsilon(p') - \xi_{\alpha}(k-P) + \hbar \omega - \epsilon(p)) \]  \hspace{1cm} (6.22)
\[ n_\alpha (k) \rightarrow n_\alpha (k-P) \]  \hspace{1cm} (6.23)

For all situations of interest \( P \ll k_{\text{thermal}} \). For a plasma of 10 ev. and excitation energy 10 ev. \( P/k_{\text{thermal}} < 2 \times 10^{-4} \). Thus, in these two functions set \( \epsilon_\alpha (k-P) \rightarrow \epsilon_\alpha (k) \).

With the above changes,

\[ \Gamma_\alpha = \int \frac{d^3p}{(2\pi)^3} \mu(p) \left\langle Q_\alpha (p) \right\rangle 
\]

\[ \left\langle Q_\alpha (p) \right\rangle = n_\alpha / \lambda_\alpha \left( G_{\eta}(k-P, \hbar \omega, k) \right) \]

\[ \times \int \frac{d^3k'}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} (2\pi \hbar \omega_k) \delta (\epsilon_\alpha (k') + \epsilon(p') - \epsilon_\alpha (k) - \hbar \omega - \epsilon(p)) \]

\[ \times (2\pi)^3 \delta (k' + p' - k - p) \sum_{m_\rho, m_\alpha} \left| \left\langle k, \beta, m_\rho | T (\epsilon_\alpha (k'), \epsilon(p)) | k', \beta' \right\rangle \right|^2 \]

\[ \times \frac{1}{2} \sum_{\delta_m} \sum_{m_\alpha} \left| \left\langle \rho / V, p | \hat{E}_\lambda \right\rangle \right|^2 \]

Compare this expression with Eqs. (6.8) and (6.9). Due to the simple form of the de-excitation probability there, only the resonance factor is involved in the thermal average. Here both the resonance factor and the de-excitation probability must be averaged together since the de-excitation amplitude is dependent on \( k \). To relate this expression to the analogous beam experiment
it is necessary to approximate the average of the product of these functions by the product of the averages. Such a procedure is reasonable in two limiting cases:

1. the absorbing atom is massive compared to the quenching atom, indicating a weak dependence on $k$ in the second factor (He - Hg, for example), or

2. Doppler shifting is negligible compared to pressure broadening, and the broadening particles engage in collisions in which the momentum of the target is unimportant (i.e., plasma quenching particles are electrons).

For these limiting situations, $P_Q(P) =$

$$
\int \frac{d^3 \rho}{4\pi^2} \left| \left\langle G \left( \frac{\rho}{\rho_0} \right) \left( \epsilon \left( k' \right) + \frac{\hbar}{\epsilon} \omega \right) \right\rangle \right|^2 \int \frac{d^3 k'}{4\pi^2} \frac{d^3 P}{4\pi^2} n(k) n(k') (6.26)
$$

$$
\times \int d^3 k' \left| \left\langle \epsilon \left( k' \right) + \epsilon \left( P' \right) - \epsilon \left( k \right) - \hbar \omega - \epsilon \left( \rho \right) \right\rangle \right|^2
\times \int d^3 \rho' \delta \left( k' + P' - k - \rho \right) \sum_{\mathbf{m}_P, \mathbf{m}_Q} \left| \left\langle k, \rho \mid T^* \left( \epsilon \left( k' \right) + \epsilon \left( P' \right) \right) \right| k', \rho' \right|^2
$$

where an average over $\rho$ has been taken. Such an average has no effect on $P_Q$. Since the first factor must also be independent of beam direction, this average may be taken to act on the absorption probability. Then, this last factor is independent of $M_\rho$, and the sum applies only to the collision probability factor.
Finally, the contribution to the total absorption rate from quenching may be written:

\[
\sigma_Q(p) = \frac{\pi}{4} \frac{e^{\beta \hbar \omega}}{\hbar} \left\langle \left( \frac{G(k, p, k', p')}{z_p / z_p'} \frac{\epsilon_\alpha(k - p) + \hbar \omega}{\hbar \omega, k} \right)^2 \right\rangle
\]

where the excitation cross-section,

\[
\sigma_{ex}(k, p') = \frac{(2\pi)^4}{\hbar k - \hbar k'} \int \frac{d^3 p}{(2\pi)^3} \frac{d^3 k}{(2\pi)^3} \delta(\epsilon_\alpha(k') + \epsilon(p') - \epsilon(k) - \hbar \omega - \epsilon(p))
\]

\[
x \delta(k' + p' - k - p) \sum_{\mu, s, s'} \left| \langle k, p | T^\mu \epsilon_\alpha(k') \epsilon(p') | k', p' \rangle \right|^2
\]

\[
\eta_\alpha(k, p) = \eta_\alpha(k') \eta(p') e^{\beta \hbar \omega}
\]

has been used in Eq. (6.27).

Thus, as one might intuitively expect, it is possible to write the partial rates as the product of an excitation probability and a de-excitation probability into a particular final channel.
However, it is clear from the above discussion that this result is by no means general; it requires a number of simplifying assumptions.

C. Total Absorption Rate and Branching Ratio

Common to $\sigma_P^{(0)}(P)$ and $\sigma_Q(P)$ is a factor which contains the details of the pressure broadening aspect of the absorption line problem. It is useful to determine to what extent this quantity may be related to the absorption line. As discussed on page 39, the total absorption rate is proportional to the discontinuity of the amplitude of Fig. 11 in the limit that broadening in the lower level may be ignored. It follows that:

$$
\Gamma_T = - I_m \sum_{\alpha} \sum_{k} \sum_{\lambda} \sum_{m_u, m_r} \langle \alpha | J^2 \xi^2 \xi \lambda \rangle \langle \xi \lambda | \alpha \rangle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle \langle \alpha | J^2 \xi^2 \xi \lambda \rangle \langle \xi \lambda | \alpha \rangle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle$$

(6.30)

As discussed on page 45 Eq. (6.30) may be approximated as:

$$
\Gamma_T = - I_m \sum_{\alpha} \sum_{\lambda} \langle \alpha | J^2 \xi^2 \xi \lambda \rangle \langle \xi \lambda | \alpha \rangle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle \langle \alpha | J^2 \xi^2 \xi \lambda \rangle \langle \xi \lambda | \alpha \rangle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle$$

(6.31)

The total absorption rate then becomes:

$$
\sigma_T = - \frac{1}{2} \left( \frac{\mu(\alpha)}{\mu(\alpha)} \right) \sigma_P^{(0)}(P) \alpha \left[ - 2 I_m \langle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle \langle \alpha | J^2 \xi^2 \xi \lambda \rangle \langle \xi \lambda | \alpha \rangle G^*(\xi \lambda) + \hbar \omega^*, L + P \rangle \langle \xi \lambda \alpha \rangle \right]$$

(6.32)
As discussed in Appendix III,

\[
\hat{\Sigma}_{E_B}^{(T)}(\epsilon_{\alpha}(K) + i\omega, K + P) = \left[ \epsilon_{\alpha}(K) + i\omega - \epsilon_{\beta}(K + P) - \langle J_{p}^{T} z_{p}^{T} | \hat{\Phi}_{E_B}^{+}(K + P) | J_{p}^{T} z_{p} \rangle \right]^{-1}
\]  \hspace{1cm} (6.33)

where \( \hat{\Sigma}_{E_B}^{(T)} \) is an \( E_B \)-proper self-energy operator, i.e., in diagram expansions for its matrix elements no single atom line labeled by a state with energy \( E_B \) is allowed.

As is well-known,

\[
\langle J_{p}^{T} z_{p}^{T} | \hat{\Phi}_{E_B}^{+} | J_{p}^{T} z_{p} \rangle = \langle J_{p}^{T} z_{p} | R_{E_B}^{+} | J_{p}^{T} z_{p} \rangle - i \langle J_{p}^{T} z_{p} | I_{E_B}^{+} | J_{p}^{T} z_{p} \rangle
\]  \hspace{1cm} (6.34)

where

\[
\langle J_{p}^{T} z_{p} | R_{E_B}^{+} | J_{p}^{T} z_{p} \rangle = \Delta_{p}(\omega, K)
\]  \hspace{1cm} (6.35)

\[
\langle J_{p}^{T} z_{p} | I_{E_B}^{+} | J_{p}^{T} z_{p} \rangle = \Gamma_{p}^{T}(\omega, K) \geq 0
\]  \hspace{1cm} (6.36)

Equation (6.32) becomes:

\[
\sigma_{T}(P) = \frac{1}{2} \left( \frac{P}{P^{2}} \right) \mu(P) \Gamma_{\alpha}(P) \left( \frac{\Gamma_{p}^{T}(\epsilon_{\alpha}(K) + i\omega, K + P)}{[\epsilon_{p}(K + P) - \epsilon_{\alpha}(K) - \Delta_{p}^{T}]^{2} + \Gamma_{p}^{T}} \right)
\]  \hspace{1cm} (6.37)

\[
= \frac{1}{2} \left( \frac{P}{P^{2}} \right) \mu(P) \Gamma_{\alpha}(P) A_{\alpha}(\omega)
\]
The effect of Doppler shifting may be explicitly shown in Eq. (6.37). Set \( \epsilon_\beta(k + P) - \epsilon_\alpha(k) = \hbar \omega_\alpha + \hbar^2 \frac{k \cdot P}{M} \).

The z-axis is taken along \( P \). Then,

\[
A_{qP}(\omega) = \int \gamma \delta(\gamma - \gamma_P) \left\langle \frac{\int \delta(\epsilon_\alpha(k) + k \omega + k \cdot P)}{\epsilon(k)(\omega - \omega_{\text{cm}} - \Delta_\rho)^2 + \gamma_{\rho}^2} \right\rangle (6.38)
\]

or

\[
A_{qP}(\omega) = \int \frac{d^3 k}{(2\pi)^3} e^{-\frac{i k \cdot L}{\hbar}} \left\langle \frac{\rho^2}{\epsilon(k)(\omega - \omega_{\text{cm}} - P/\hbar - \Delta_\rho)^2 + \gamma_{\rho}^2} \right\rangle (6.39)
\]

The bracket in Eq. (6.39) means averaging with

\[
\int \frac{d^3 k}{(2\pi)^3} e^{i (\mathbf{k} \cdot \mathbf{x} - \mathbf{e} \cdot \mathbf{x})}
\]

If the self-energy function is only weakly dependent on c.m. momentum of the atom, the above expression is the basis for the simple "folding-in" procedure often utilized to account for Doppler shifting.

It is important to note that nothing has been said about the specific nature of the collisions up to now. For example, in a hydrogen plasma the effects of both electrons and ions must be
considered simultaneously; i.e., no "impact" approximation has been applied here. If, however, the self-energy is only weakly dependent on the frequency of the incident light, then the expression above represents a Lorentzian line shape where $\Gamma_B$ is a measure of the width of the line.

To relate $\sigma_T(P)$ to the expressions for $\sigma_Q(P)$ and $\sigma_p(P)$, it is necessary to approximate the averaging over the atom's c.m. momentum according to the technique used for $\sigma_Q(P)$. Then,

$$
\sigma_T(P) = \frac{n \epsilon}{x} \left( \frac{\mu(k)}{\mu(k')} \right) \exp \left( \frac{i}{\hbar} \kappa \omega \frac{k}{k'} P \right) \left\langle \left( \frac{C^{(p)}}{C^{(p')}} \right) \left( \frac{C^{(p')}}{C^{(p)}} \right) \right\rangle_{Z^T} \left( \frac{\epsilon}{\hbar} \kappa \omega \right) \left( \frac{k}{k'} \right) P \right\rangle_{Z^T}^{-1}
$$

Comparison with Eq. (6.27) gives:

$$
\sigma_Q(P) \sigma_T(P) = n \left( \frac{\mu(k)}{\mu(k')} \right) \exp \left( \frac{i}{\hbar} \kappa \omega \frac{k}{k'} P \right) \left\langle \left( \frac{C^{(p)}}{C^{(p')}} \right) \left( \frac{C^{(p')}}{C^{(p)}} \right) \right\rangle_{Z^T} \left( \frac{\epsilon}{\hbar} \kappa \omega \right) \left( \frac{k}{k'} \right) P \right\rangle_{Z^T}^{-1}
$$

where $n$ is the number/volume of quenching particles. The brackets in both Eqs. (6.40) and (6.41) denote averages over c.m. momentum of the atom and the quenching particle. The branching ratio for de-excitation by collision or radiation is then determined.

In the even that $\Gamma_B$ is not a sensitive function of the
incident energy or the c.m. momentum of the atom, it is precisely the full-width at half maximum of the absorption line. The branching ratio is then determined by quantities directly accessible to experiment.

To get an idea of the branching ratio for a particular system consider the Ly-α line of atomic hydrogen in a plasma. Since the total cross-section is a Lorentz invariant,

$$
\frac{d^2K'}{d\Omega} \eta(k') v' \sigma^{(k')} (k', p') = \int \frac{d^2K}{d\Omega} \eta(k) v \sigma^{(k)} (k, p) \quad (6.42)
$$

where negligible corrections to the statistical factor have been ignored. Note that the cross-section is dependent only on the energy of the electron in the rest frame of the atom. Then,

$$
\frac{\sigma_\Omega}{\sigma_T} = \frac{e^{2\pi \mu^2/\Omega} \Gamma(\mu)}{\Gamma(\mu)} e^{-\mu^2/\Omega} \int dy \int \frac{\eta}{v} e^{-y \sigma_\Omega(y)} \quad (6.43)
$$

where for the Ly-α line of hydrogen $\mu(\beta)/\mu(\alpha) = 3$, and $\Gamma(\text{Ly-α})$ is the full-width at half maximum of the absorption line.

$$
X_{T} = \frac{h}{\eta(\Omega)^{1/2}}, \quad \frac{E_\omega}{h} = \frac{\omega_\text{p}}{h}
$$

the frequency of the line, $V = \text{volume/electron}$, and $\pi a_0^2$ is the
cross-sectional area of the first Bohr orbit. For calculational convenience a dimensionless measure of the cross-section has been introduced:

$$ \sigma(\varepsilon)(e) = \frac{1}{\varepsilon} \sigma_0(y), \quad y = \varepsilon/\theta $$

(6.44)

For $T = 40,000$ K, $n = 10^{19}$ electrons/cm.$^3$, $\Gamma(\text{Ly-}\alpha) = 0.017$ ev.$^{11}$ From experimental data on electron excitation of the Ly-\( \alpha \) line$^{12}$ numerical integration gives

$$ \int dy y e^{-\frac{y}{\theta}} \sigma_0(y) = 0.023 $$

The value of the integral is essentially determined by the threshold data, the exponential factor providing a strong cutoff. Then

$$ \sigma_Q/\sigma_T = 0.019 \text{ or } \gamma(P) = 0.02. $$

The branching ratio is defined as:

$$ \gamma(P) = \sigma_Q/\sigma_T = \left(\frac{\sigma_T}{\sigma_Q}\right)^{-1} $$

(6.45)

From the above it is clear that pure quenching is a relatively unimportant mechanism for the de-excitation of the atom in this example.

For the case in which quenching particle is identical to the absorbing atom, the quenching rate is usually a significant part of the total rate.$^6$
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APPENDIX A. Analytic Continuation and Frequency Sums for Total Absorption Rate Calculation

1. Special Case

The first diagram of the ladder sequence for the special case involves the sum,

\[ \sum_{\omega_n} G_{\alpha\alpha}(k, \omega_n) G_{\beta\bar{\beta}}(k+P, \omega_n + \omega) \]  

(A.1)

over frequencies

\[ \omega_n = i (2n+1) \pi/\beta. \]

This sum is reproduced by the contour integral

\[ \frac{1}{2\pi i} \int_{c} dz G_{\alpha\alpha}(k, z) G_{\beta\bar{\beta}}(k+P, z + \omega) \]  

(A.2)

with the contour surrounding the poles of

\[ f(z) = \left[ e^{iz} + 1 \right]^{-1} \]  

(A.3)

for \( z = \omega \), with residue \(- (\beta)^{-1}\). (See Fig. 17a.) Take \( \text{Im} \omega > 0 \). In accordance with the well-known analytic structure of the one-particle propagator, the branch cuts at \( \text{Im} z = 0 \) for \( G_{\alpha\alpha}(z) \) and at \( \text{Im}(z + \omega) = 0 \) for \( G_{\beta\bar{\beta}}(z + \omega) \) are explicitly shown.
Figure 17.
It is convenient to distort the contour \( \Gamma_0 \to \Gamma \) to facilitate the integration. The integral becomes:

\[
\frac{1}{2\pi i} \left\{ \int_{-\infty}^{\infty} dx \, f_+(x) G_{\alpha\kappa}(x-i\gamma) G_{\rho\sigma}(x-i\gamma+i\omega) \\
- \int_{-\infty}^{\infty} dx \, f_+(x) G_{\alpha\kappa}(x+i\gamma) G_{\rho\sigma}(x+i\gamma+i\omega) \\
+ \int_{-\infty}^{\infty} dx \, f_+(x-\omega_n) G_{\alpha\kappa}(x-i\gamma-\omega_n) G_{\rho\sigma}(x-i\gamma) \\
- \int_{-\infty}^{\infty} dx \, f_+(x-\omega_n) G_{\alpha\kappa}(x+i\gamma-\omega_n) G_{\rho\sigma}(x+i\gamma) \right\}
\]  

(A.4)

To perform the analytic continuation set \( f_+(x-\omega_n) = f_+(x) \) then \( \omega_n\to\omega+ie \) where \( e>\eta \). In the third and fourth integrals set \( x \to x+\omega \). Equation (A.4) then becomes:

\[
\frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left[ f_+(x) - f_+(x+\omega) \right] R_\pm + \frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left[ f_+(x+\omega) R_\pm - f_+(x) R_\pm \right] \]  

(A.5)

where

\[
R_\pm = G_{\alpha\kappa}(x-i\gamma, \kappa, \rho) G_{\rho\sigma}(x+\omega+i\gamma, \kappa, \rho) \]  

(A.6)

\[
R_\pm = G_{\alpha\kappa}(x+i\gamma, \kappa, \rho) G_{\rho\sigma}(x+\omega+i\gamma, \kappa, \rho) \]  

(A.7)

It is convenient to write
\[ R_{+-} = (\chi_+ - \Delta \chi^{('n)}_+)^{-1} (\chi_- - \Delta \chi^{('2)}_-)^{-1} \]

\[ = (\Delta \chi^{('n)}_+ - \Delta \chi^{('2)}_-)^{-1} (\chi_+ - \Delta \chi^{('n)}_+)^{-1} (\chi_- - \Delta \chi^{('2)}_-)^{-1} \]  

(A.8)

with

\[ \Delta \chi^{('n)}_+ \equiv \langle \alpha_1 | \Psi^+ (\chi, \kappa) | \kappa \rangle \]

(A.9)

\[ \Delta \chi^{('2)}_- \equiv \langle \beta_1 | \Psi^+ (\chi+\omega, \kappa+\kappa') | \beta \rangle \]

\[ + \left( \varepsilon_d (\kappa+\kappa') - \varepsilon_d (\kappa) - i\omega \right) \]

(A.10)

\[ \chi_+ \equiv \chi \pm i\gamma + \mu a_{-} - \varepsilon_d (\kappa) \]

(A.11)

Upon expanding the two terms in the second bracket in the neighborhood of

\[ \Delta \chi^{('n)}_+ \Delta \chi^{('2)}_- = 0 \]  

(A.12)

\[ R_{+-} = \left( \frac{1}{\chi} \right)^+ \cdots \]  

(A.13)

Similarly,
\[
R_{\pm} = (\Delta \chi_-^{(n)} - \Delta \chi_+^{(n)})^{-1} (\chi_- - \Delta \chi_-^{(n)})^{-1} (\chi_+ - \Delta \chi_+^{(n)})^{-1}
\]
\[
= 2\pi i \delta(\chi) (\Delta \chi_-^{(n)} - \Delta \chi_+^{(n)})^{-1} + (\Delta \chi_-^{(n)} - \Delta \chi_+^{(n)})^{-1} \times \left( \frac{\Delta \chi_-^{(n)}}{\chi_-^2} - \frac{\Delta \chi_+^{(n)}}{\chi_+^2} + \ldots \right) \quad \text{(A.14)}
\]

These expansions are divergent for \( \chi = 0 \), but their validity rests on the slow dependence of all quantities on the momentum of the atom and the final integration over this variable.

From the expansions above it is clear that the dominate contribution to the frequency sum comes from the first integral in Eq. (A.5). If the smaller contributions are neglected, Eq. (A.5) becomes:

\[
(f_+ (\epsilon_\alpha (k_i) - \mu \omega) - f_+ (\epsilon_\alpha (k_i^0) - \mu \omega + \hbar \omega))
\]
\[
\times \left[ \hbar \omega - (\epsilon_\alpha (k_i^0, p) - \epsilon_\alpha (k_i)) - \langle \phi | \Phi (\epsilon_\alpha (k_i) - \mu \omega + \hbar \omega, k_i^0 + p) | \phi \rangle - \langle \phi | \Phi^- (\epsilon_\alpha (k_i) - \mu \omega, k_i | k_i) \rangle \right]^{-1} \quad \text{(A.15)}
\]

In the spirit of the impulse approximation, only on-energy-shell scattering amplitudes should figure into the determination of the self-energy functions. If self-energy functions are smoothly varying functions of energy and sufficiently small, one may evaluate them for \( \epsilon_\alpha (k_\perp) + \omega \rightarrow \epsilon_\beta (k_\perp + p) \). A
similar approximation for the second statistical term of Eq. (A.15) gives:

\[
\begin{align*}
\mathcal{F}_+(\epsilon\zeta(K)-\mu) & - \mathcal{F}_+(\epsilon\zeta(K)-\mu) + \mathcal{F}_+(\epsilon\zeta(K)-\mu) + \mathcal{F}_+(\epsilon\zeta(K)-\mu) \\
\rightarrow \eta_{\alpha}(K) - \eta_{\rho}(K+p) & = \eta_{\alpha}(K)(1-\eta_{\rho}(K+p))(1-e^{-i\omega})
\end{align*}
\]  

(A.16)

With these approximations Eq. (4.4) becomes:

\[
\begin{align*}
(e^{-i\omega} - 1) \int \frac{d^3k}{(2\pi)^3} & \sum_{\alpha} \eta_{\alpha}(K)(1-\eta_{\rho}(K+p)) \\
\times \langle \alpha | \mathcal{P}^+ \mathcal{P}^- | \beta \rangle & \[\omega - (\epsilon_{\rho}(K+p) - \epsilon_{\alpha}(K)) - \langle \alpha | \mathcal{P}^+ \mathcal{P}^- | \beta \rangle \\
& - \langle \alpha | \mathcal{P}^+ \mathcal{P}^- | \beta \rangle \langle \beta | \mathcal{P}^+ \mathcal{P}^- | \alpha \rangle 
\end{align*}
\]  

(A.17)

where

\[
\begin{align*}
\langle \gamma | \mathcal{P}^+ \mathcal{P}^- (K) | \gamma \rangle & = \langle \gamma | \mathcal{P}^+ (\nu \pm i\gamma, K) | \gamma \rangle \\
\nu & = \epsilon_{\gamma}(K) - \mu
\end{align*}
\]  

(A.18)

To calculate the full ladder sequence it is necessary to explicitly perform the frequency sums of Eq. (4.12). The gas particle frequency sum is converted into a contour integral surrounding the poles of \( f_+(z) \) in the usual manner:
Thus, the final frequency sum becomes:

\[
\frac{1}{\beta} \sum_{\omega_{m1}} G^{(o)}(\omega_{m} + \omega_{m1} - \omega_{m2}, \mu_{a}, \beta, z) G^{(o)}(\omega_{m1}, \mu, z) = \rightangle \text{Residue} \left[ f_{+}(z) G^{(o)}(\omega_{m} + z - \omega_{m2}, \mu_{a}, \beta, z + 2) G^{(o)}(z, \mu, \beta) \right] = \]

\[
[f_{+}(\epsilon + z + \mu_{a}) - f_{+}(\epsilon + \mu)] G^{(o)}(\epsilon + z + \mu_{a} - \omega_{m} + \omega_{m1} - \omega_{m2} + \omega_{m}, \mu, \beta, z) \]  

(A.19)

which is equivalent to:

\[
\frac{1}{\beta} \sum_{\omega_{m2}} G_{\alpha_{2} \alpha_{2} \beta_{2}}(\omega_{m2}, \beta, \lambda_{\alpha_{2} \beta_{2} \lambda_{2} \beta_{1}}) \Lambda_{\alpha_{3} \alpha_{4} \lambda_{3} \beta_{4}}(\omega_{m1}, \omega_{m} + \omega_{m2}) \times G_{\gamma_{2} \gamma_{2} \delta_{2}}(\omega_{m2} + \omega_{m}, \beta + \gamma) G^{(o)}(\epsilon + z + \mu_{a} - \omega_{m} + \omega_{m1} - \omega_{m2} + \omega_{m}, \mu, \beta, z) \]

(A.20)

where \( \Gamma_{0} \) is the contour of Fig. 17a. In anticipation of the distortion of the contour, \( \Gamma_{0} \rightarrow \Gamma \), note that the second factor in the above integral has:
1. a branch discontinuity for \( \text{Im } z = 0 \),
2. a branch discontinuity for \( \text{Im } (z + \omega_n) = 0 \) and
3. a simple pole for \( z + \epsilon(p_1 + q) - \omega_n - \epsilon(p_1) = 0 \),
if \( A \) is assumed to have the analytic structure expressed by
1. and 2. That \( A \) does have such a structure follows directly
from the iteration equation which it satisfies. The first
factor in the contour integral has been chosen in such a way that the
simple pole gives no contribution for the \( \Gamma \) contour of Fig. 17b.
As in Eq. (A.4), integration along the \( \Gamma \) contour gives:

\[
\frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left( f(x) + \epsilon \right) G^{(0)}(x - \omega_n + \epsilon(p_1 + q) - \mu_1) G_{\alpha \beta} p_2 (x + \omega_n)
\]

\[
\times \left[ G_{\alpha \beta} \mu_1 \Lambda_{\alpha_1 \beta_1} \Lambda_2 \beta_2 \left( x - \omega_n + \epsilon(p_1 + q) - \mu_1 \right) G_{\alpha \beta} \mu_1 \Lambda_{\alpha_1 \beta_1} \Lambda_2 \beta_2 \left( x + \omega_n \right) \right]
\]

\[
\frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left( f(x) + \epsilon \right) G^{(0)}(x - \omega_n - \omega_n + \epsilon(p_1 + q) - \mu_1) G_{\alpha \beta} \mu_1 \Lambda_{\alpha_1 \beta_1} \Lambda_2 \beta_2 \left( x - \omega_n \right)
\]

\[
\times \left[ G_{\alpha \beta} \mu_1 \Lambda_{\alpha_1 \beta_1} \Lambda_2 \beta_2 \left( x - \omega_n + \epsilon(p_1 + q) - \mu_1 \right) G_{\alpha \beta} \mu_1 \Lambda_{\alpha_1 \beta_1} \Lambda_2 \beta_2 \left( x - \omega_n \right) \right]
\]

where the momentum dependence has been suppressed for convenience.

The analytic continuation of \( A \) has three separate pieces:

\[
\omega_n \rightarrow z + i \epsilon, \quad \omega_n + \omega_n \rightarrow z + \omega + i \epsilon
\]
where

\[
(\varepsilon_1, \varepsilon_2) = \begin{pmatrix}
-1, -1 \\
-1, +1 \\
+1, +1
\end{pmatrix}
\]  \hspace{1cm} (A.24)

Let

\[
\sqrt{(z + i\eta_1 \omega + i\eta_2 \omega)}, \quad \eta_1, \eta_2 = \mp 1
\]

represent the various analytic functions defined by Eq. (A.22). Then,

\[
\sqrt{(z + i\eta_1 \omega + i\eta_2 \omega)} = \frac{i}{\pi} \int_0^\infty d\omega \left[ (f^+(\omega) + f^-) G^{(0)}(x - z - i\omega_0 + \epsilon \omega + \mu \omega) - (f^+(\omega) + f^-) G^{(0)}(x - z - i\omega_0 + \epsilon \omega + \mu \omega) \right] G_{\eta_1 \eta_2}^{(x)}(x - \omega)
\]

\[
\times G_{\eta_1 \eta_2}^{(x)}(x + \omega + i\omega) \Lambda \alpha \beta \gamma (x + \omega + i\omega) + i\eta_1 \int_0^\infty d\omega \left[ (f^+(\omega) + f^-) G^{(0)}(x - z - i\omega_0 + \epsilon \omega + \mu \omega) \right] \Lambda \alpha \beta \gamma (x - \omega + \omega - i\omega)
\]

\[
\times G_{\eta_1 \eta_2}^{(x)}(x - i\omega_0) G_{\eta_1 \eta_2}^{(x + \omega - i\omega_0)} \Lambda \alpha \beta \gamma (x - i\omega_0) \Lambda \alpha \beta \gamma (x + \omega - i\omega_0)
\]

\[
- \frac{i}{\pi} \int_0^\infty d\omega \left[ (f^+(\omega) + f^-) G^{(0)}(x - z - i\omega_0 + \epsilon \omega + \mu \omega) \right] \Lambda \alpha \beta \gamma (x + i\omega) \Lambda \alpha \beta \gamma (x + i\omega + i\omega)
\]

\[
\times G_{\eta_1 \eta_2}^{(x)}(x + i\omega) G_{\eta_1 \eta_2}^{(x + \omega + i\omega)} \Lambda \alpha \beta \gamma (x + i\omega) \Lambda \alpha \beta \gamma (x + \omega + i\omega).
\]
This equation should be compared with Eq. (A.4). The same expansion procedure used there indicates that \( V \) is correctly represented in the same approximation by the first integral of Eq. (A.25).

For \( A \) this result implies that

\[
\begin{align*}
\Lambda_{\alpha_{1}, \beta_{1}}^{\gamma_{1}} \left( K_{1}, z + \eta_{1} \mid K + p, z + \omega + \eta_{2} \right) &= \delta_{\alpha_{1} \beta_{1}}^{\gamma_{1}} \delta_{p}^{p}, \\
- \sum_{K_{1}} \int \frac{d^{3} K_{1}}{(2 \pi)^{3}} \int \frac{d^{3} P_{1}}{(2 \pi)^{3}} (n(P_{1} + q) - n(P_{1})) \left( \alpha_{1} K_{1}, P_{1} + p \mid V \mid \alpha', K \right) \\
x \left( \beta_{1} P + K, P_{1} \right) & \left( \eta_{1}, \epsilon_{1}, \epsilon_{2}, \rho, \gamma_{1}, \eta_{2} \right) \int_{-\infty}^{\infty} dx \left[ \left( f(x) + f(-x) \right) \right] \\
x G^{(2)}(x - z - i \gamma_{1} \omega + \epsilon_{1} - \epsilon_{2}, \rho, \gamma_{1}, \eta_{2}) - (f(x + i \omega) + f(-x + i \omega)) \\
x G^{(2)}(x - z - i \gamma_{1} \omega + \epsilon_{1} - \epsilon_{2}, \rho, \gamma_{1}, \eta_{2}) \delta(x + \mu_{1} - \epsilon_{2}(k_{1})) \\
x \Lambda_{\alpha_{1}, \beta_{1}}^{\gamma_{1}} \left( K_{1}, x - i \omega \mid K_{2} + P, x + \omega + i \omega \right) \\
x \left[ \omega - (\epsilon_{2}(K_{2} + P) - \epsilon_{2}(K_{1})) - (\langle \rho \mid F^{T}(x + \omega, K_{2} + P) \rangle_{\theta} - \langle \theta \mid F^{T}(x, K_{2}) \rangle_{\theta} \right]^{\gamma_{1}}.
\end{align*}
\]
From this equation the various branches of $A$ may be determined.

The "ladder" approximation for $\hat{A}(p, \omega)$ may be written:

$$
- \sum_{\alpha', \beta'} \int_{\frac{-2i\pi}{\Delta}} \frac{d^3k}{(2\pi)^3} \frac{1}{2\pi i} \int_0^\infty f_+ (z) \langle \alpha | \mathcal{V} \rho | \beta \rangle G_{\alpha \beta} (z) G_{\alpha' \beta'} (z + \omega_n) \tag{A.27}
$$

$$
\times \left| \xi \right| \left| \xi' \right| (z/(z + \omega_n)) \langle \theta | \mathcal{V} | \theta' \rangle
$$

where $\Gamma_0$ is the contour of Fig. 17a. With the contour $\Gamma$ the integral is:

$$
\frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left( f_+ (x) - f_+ (x + \omega) \right) G_{\alpha \beta} (x + i\omega + i\delta) \Lambda_{\alpha \beta} \Lambda_{\alpha' \beta'} (x + i\omega + i\delta)
$$

$$
+ \frac{1}{2\pi i} \int_{-\infty}^{\infty} dx f_+ (x + \omega) G_{\alpha \beta} (x + i\omega - i\delta) \Lambda_{\alpha \beta} \Lambda_{\alpha' \beta'} (x + i\omega - i\delta)
$$

$$
- \frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \langle f_+ (x) G_{\alpha \beta} (x + i\omega) G_{\alpha' \beta'} (x + i\omega + i\delta) \Lambda_{\alpha \beta} \Lambda_{\alpha' \beta'} (x + i\omega + i\delta).
$$

Again ignoring all but the contribution of the first integral of Eq. (A.28) evaluated in the approximate fashion illustrated above for $A$, one finds:
\[ \Phi(P, \omega) = \sum_{i=0}^{\infty} \frac{1}{\omega_i} \int_{\omega_i}^{\omega_{i+1}} \int d^3k \langle f_+^*(x) - f_-(x+\omega) \rangle \delta(x+\mu_k - \epsilon_k(k)) \]

\[ \times \left\langle \left( \frac{1}{E} \right)^2 \right\rangle \left( \frac{1}{E_k} \right) \left\langle \left( \frac{1}{E_k+\omega} \right)^2 \right\rangle \left( \frac{1}{E_k+\omega+\delta} \right)^2 \left( \frac{1}{E_k+\omega+\delta+\epsilon} \right)^2 \]

(A.29)

\[ x \left[ \frac{\hbar \omega}{(\epsilon_k(k_1) - \epsilon_x(k_1)) - \left( \langle \Phi_+^* \epsilon_k(k_1, k, 1) \rangle \right)^{-1} \left( \langle \Phi_+^* \epsilon_k(k_1, k, 1) \rangle \right)^{-1} \right] \]

If the resonance is sharp and both \( \Lambda^+ \) and \( \phi^+ \) are smooth functions of frequency, one may substitute for these quantities as arbitrary functions of frequency their values for \( \omega + \epsilon_k(k_1) = \epsilon_p(k_1 + P) \).

The same expressions are used with the frequency dependence suppressed.

The statistical factors appearing in Eq. (A.29) are conveniently rearranged as:

\[ (n(p) - n(p+9))(n_x^2(k_2) + \left( e^{\frac{\epsilon(p) - \epsilon(p+9)}{\epsilon(p)}} - 1 \right)^{-1}) \]

\[ = -n(p)(1-n_x^2(k_2)) \left( 1-n(p+9) \right) \left( 1-e^{\frac{\epsilon(p) - \epsilon_x(k_2)}{\epsilon(p)}} \right) \left( e^{\frac{\epsilon(p) - \epsilon_x(k_2)}{\epsilon(p)}} - e^{\epsilon(p+9)} \right) \]

(A.30)

with a similar expression for the second statistical factor.

Finally, in the low density limit for absorbing atoms:
1 - \eta_c(\mu_e - \epsilon_e(\beta)) \to 0 \quad (A.31)

\Phi(P,\omega) = (e^{-i\omega t} - 1) \sum_{\alpha} \int \frac{d^3k}{(2\pi)^3} \eta_\alpha(k) (1 - \eta_\rho(k + P))

\times \langle \alpha | i \hat{\mathcal{E}} | \beta \rangle \ \Lambda^{--}_{\alpha \beta} (k, k + P) \langle \beta | i \hat{\mathcal{E}}^* | \alpha \rangle

\times \left[ \pi \omega - (\epsilon_\alpha(k + P) - \epsilon_\alpha(k)) - (\langle \beta | \Phi^+ | k + P \rangle | \beta \rangle - \langle \alpha | \Phi^* | k \rangle | \alpha \rangle \right]^{-1}

where \( \Lambda^{--} \) satisfies the equation:

\quad \Lambda^{--}_{\alpha \beta}(k, k + P) = \delta_{\alpha \beta} \delta(k + P, k)

\quad = - \sum_{\alpha \beta} \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} \eta_\alpha(k) (1 - \eta_\rho(k + q))

\times 2\pi i \delta (\epsilon_\alpha(k) - \epsilon_\alpha(k) + \epsilon(q) - \epsilon(P + q)) \langle k_2, k_1, P + q | V | k_1, k_2, P \rangle

\times \langle P + k_1, P | \mathcal{V} | k_2, k_1, P + q \rangle \ \Lambda^{--}_{\alpha \beta}(k, k + P)

\times \left[ \pi \omega - (\epsilon_\alpha(k + P) - \epsilon_\alpha(k)) - (\langle \beta | \Phi^+ | k + P \rangle | \beta \rangle - \langle \alpha | \Phi^* | k \rangle | \alpha \rangle \right]^{-1}
2. The General Case

In the general case consider Eq. (4.3). The frequency sum may be performed in the same way as with Eq. (A.2). That is,

\[
\frac{1}{\pi i} \int_{-\infty}^{\infty} dx f(x) f(x+\omega) R_{-+} + \frac{1}{\pi i} \int_{-\infty}^{\infty} dx f(x) f(x-\omega) R_{+-} + \frac{1}{\pi i} \int_{-\infty}^{\infty} dx f(x) f(x+\omega) R_{-+} = (A.34)
\]

where as before:

\[
R_{-+} = G_{\kappa \kappa'} (x-i\eta, \kappa, \bar{\kappa}) G_{\bar{\kappa} \bar{\kappa}''} (x+i\eta, \bar{\kappa}, \bar{\kappa}'') \quad (A.35)
\]

\[
R_{++} = G_{\kappa \kappa'} (x+i\eta, \kappa, \bar{\kappa}) G_{\bar{\kappa} \bar{\kappa}''} (x-i\eta, \bar{\kappa}, \bar{\kappa}'') \quad (A.36)
\]

The first integral of Eq. (A.34) gives the main contribution as discussed repeatedly above. \( G_{\gamma \gamma'} (\omega, \kappa) \) is to be regarded as the matrix elements of the operator \( G(\omega, \kappa) \) satisfying the matrix equation,

\[
[\hbar \omega - \epsilon_a (\kappa) - H_0 + \mu_\omega - \Phi (\omega, \kappa)] G(\omega, \kappa) = \mathbb{I} \quad (A.37)
\]

where \( \epsilon_a (\kappa) \) is the kinetic energy of the atom.

Consider the eigenvalue spectrum:
\[ (H_0 + \tilde{\Phi}(x, \kappa)) | \chi_i(x, \kappa) \rangle = \nu_i(x, \kappa) | \chi_i(x, \kappa) \rangle \]  

(A.38)

Associated with the set \( \{|\chi_i(x, \kappa)\rangle\} \) is the reciprocal set \( \{|\xi_i(x, \kappa)\rangle\} \) for which
\[ \langle \xi_i(x, \kappa) | \chi_i(x, \kappa) \rangle = \delta_{ij} \]  

(A.39)

In general these eigenvectors do not constitute a complete set. However, in the limit that the \( \tilde{\Phi} \)'s constitute a small perturbation on \( H_0 \), this conclusion usually may be assumed valid. In this event \( G(x + \eta, \kappa) \) has a spectral representation:
\[ G(x+\eta, \kappa) = \sum_i \frac{|\chi_i(x, \kappa)\rangle\langle \xi_i(x, \kappa)|}{x+i\eta + \mu_a - \epsilon_a(\kappa) - \nu_i(x, \kappa)} \]  

(A.40)

and since \( \tilde{\Phi}(x, \kappa) = (\Phi^+(x, \kappa))^\dagger \),
\[ G(x-\eta, \kappa) = \sum_i \frac{|\xi_i(x, \kappa)\rangle\langle \chi_i(x, \kappa)|}{x-i\eta + \mu_a - \epsilon_a(\kappa) - \nu_i^*(x, \kappa)} \]  

(A.41)

(A.42)

With these spectral representations the frequency sum of Eq. (4.3) becomes:
Again it is necessary to approximate the product of these energy denominators. However now the procedure used previously is ambiguous since the point of expansion of the energy denominators is not unique. It is important to realize that the end result of the expansion is to uncover an energy conservation relating the integration variable and the point of expansion. Let $\Gamma$ be a measure of the expected width of a particular isolated line. If the self-energy functions are insensitive to variations in their energy over a range $\Gamma$, then the result of the expansion is clearly insensitive to the precise point of expansion. For convenience expand about $\varepsilon_\alpha$ to make easy contact with the old result.

The energy denominators may be written:

$$
\left( \chi - i\gamma + \mu a - \varepsilon_\alpha (\kappa_j) - (W_i^* (x, \kappa_j) - \varepsilon_\alpha) \right)^{-1}
$$

$$
\times \left( \chi + i\gamma + \mu a - \varepsilon_\alpha (\kappa_j) - (W_j (x+\omega, \kappa_j + \kappa) + \varepsilon_\alpha (\kappa_j + \kappa) - \varepsilon_\alpha (\kappa_j)) \right)^{-1}
$$

(A.44)
Upon expanding one obtains for the first integral of Eq. (A.34):

\[ \frac{i}{\hbar \omega} \int_{-\infty}^{\infty} dx \left( f_+^{*}(x) - f_+(x+\omega) \right) \sum_{ij} \langle \alpha' | \Sigma_i(x, k_i) \rangle \langle \Sigma_i(x, k_i) | \alpha \rangle \]

\[ \times \left( \rho \langle x+\omega, k_i, P \rangle \langle \Sigma_i(x, k_i, P) | \alpha' \rangle i \hbar \delta(x+\omega - \varepsilon(x)) \right) \]

\[ \times \left[ \frac{1}{\hbar \omega} - \left( \varepsilon(x+\omega, k_i, P) - \varepsilon(x, k_i) \right) - \left( W_i(x+\omega, k_i, P) - W_i(x, k_i) \right) \right]^{-1} \]

Equation (A.45) may then be expressed in terms of the original basis through the use of the dyad vector space introduced on page 30. One obtains for (A.45)

\[ \int_{-\infty}^{\infty} dx \left( f_+^{*}(x) - f_+(x+\omega) \right) \delta(x+\omega - \varepsilon(x)) \]

\[ \times \left( \rho \langle x+\omega, k_i, P \rangle \langle \Sigma_i(x, k_i, P) | \alpha' \rangle i \hbar \delta(x+\omega - \varepsilon(x)) \right) \]

\[ \times \left[ \frac{1}{\hbar \omega} - \left( H_k^{\rho}(x, k_i, P) - H_k^{\rho}(x, k_i) \right) - \left( \Phi^R(x+\omega, k_i, P) - \Phi^L(x, k_i) \right) \right]^{-1} \]

where, for example,

\[ \langle \alpha' | \Phi^{R} | \alpha \rangle = \delta_{\alpha\alpha'} \langle \alpha | \Phi^{L} | \alpha' \rangle \] (A.47)

From this example it is clear that the results of the special case may be transposed immediately to the general case. The only essential difference is that the equation which \( A \) satisfies involves summations over both the right and left hand sets of subscripts. One finds:
\[ \Phi (p, \omega) = (e^{-i\omega p} - 1) \sum_{\alpha, \beta} \int \frac{d^3k_1}{(2\pi)^3} \varphi_{\alpha} (k_1) \langle \alpha' | I \hat{\phi} | \beta' \rangle \]

\[ \times \langle \alpha | \left[ \frac{\omega}{\tilde{H}_{0}^{R}(k_{1} + p) - \tilde{H}_{0}^{L}(k_{1})} \right] \left[ (\Phi^{+ R}(k_{1}, p) - \Phi^{- L}(k_{1})) \right] | \beta \rangle \]

\[ \times \sum_{\alpha, \beta} \int \frac{d^3k_2}{(2\pi)^3} \int \frac{d^3p}{(2\pi)^3} \varphi_{\beta} (p) (1 - \varphi_{\beta} (p + q)) \]

\[ \times 2\pi i \delta (E_{\alpha} (k_2) + E (p + q) - E_{\beta} (k_1) - E (p)) \langle \alpha | \tilde{\alpha} \rangle \langle \beta | \tilde{\beta} \rangle \langle \tilde{\alpha} | \tilde{\beta} \rangle \]

\[ \times \langle \beta | p + k, p, 1/V | \beta' \rangle \langle \alpha' \rangle \langle \beta' | p + k + p, p + q \rangle \sum_{\beta, \alpha} \langle \beta | p + k + p, p + q \rangle \langle \alpha' | \beta' \rangle \langle \beta' | p + k + p \rangle \] (A.48)

and

\[ \sum_{\alpha, \beta} \int \frac{d^3k_2}{(2\pi)^3} \int \frac{d^3p}{(2\pi)^3} \varphi_{\beta} (p) (1 - \varphi_{\beta} (p + q)) \]

\[ \times 2\pi i \delta (E_{\alpha} (k_2) + E (p + q) - E_{\beta} (k_1) - E (p)) \langle \alpha | \tilde{\alpha} \rangle \langle \beta | \tilde{\beta} \rangle \langle \tilde{\alpha} | \tilde{\beta} \rangle \]

\[ \times \langle \beta | p + k, p, 1/V | \beta' \rangle \langle \alpha' \rangle \langle \beta' | p + k + p, p + q \rangle \sum_{\beta, \alpha} \langle \beta | p + k + p, p + q \rangle \langle \alpha' | \beta' \rangle \langle \beta' | p + k + p \rangle \] (A.49)

\[ \times \langle \alpha_{\beta_2} \rangle \left[ \tilde{\Phi} (\omega) - (\tilde{H}_{0}^{R}(k_{2} + p) - \tilde{H}_{0}^{L}(k_{2})) - (\Phi^{+ R}(k_{2} + p) - \Phi^{- L}(k_{2})) \right] \tilde{\alpha} \tilde{\beta_2} \rangle.
To put these results in a more transparent form it is convenient to define:

\[
M_{K_i}(P, \omega) = \left( \alpha_1 | \right. 
\left\langle f_0^R (k_1, k_2^R, k_3^L) | \phi_0^L (k_3) \right| f_1^L (k_4) \left| \alpha_2 \right\rangle
\]  
(A.50)

and

\[
K_{K_i} (P) = \int \frac{d^3 p_1}{(2\pi)^3} \frac{d^3 p_2}{(2\pi)^3} \, n(p_1) (1 - n(p_2)) 
\times \left( \delta (p_1 - k_1) + \delta (p_2) - \epsilon_n (k_1) - \epsilon_n (p_2) \right) \delta (k_2 + p_1 - k_3 - p_2) 
\times \left( \alpha_1 | \right. 
\left\langle f_1^R (k_2^R, k_3^L, p_3^L) | \phi_0^L (k_3) \right| f_1^L (k_4) \left| \alpha_2 \right\rangle
\]  
(A.51)

where, for example,

\[
\left( \alpha_2 | \right. 
\left\langle K_a | f_1^R (k_2^R, k_3^L, p_3^L) | \phi_0^L (k_3) \right| f_1^L (k_4) \left| \alpha_2 \right\rangle
\]  
(A.52)

Then

\[
\phi (P, \omega) = 
\left( e^{-iK^a_\omega} \right) \sum_{\alpha_1, \alpha_2} \int \frac{d^3 k_1}{(2\pi)^3} \, n_\alpha (k_1) \left( \alpha_1 | f_1^R (k_1^R, k_2^R, k_3^L) | \phi_0^L (k_3) \right| f_1^L (k_4) \left| \alpha_2 \right\rangle
\]  
(A.53)
where $\mathbf{M}^{-1} (\mathbf{P}, \omega)$ satisfies the matrix equation

$$
\left[ \begin{array}{c}
\epsilon \omega - (H_0^R (\mathbf{k}' + \mathbf{p}) - H_0^L (\mathbf{k}')) - (\mathbf{F}^+ (\mathbf{k}' + \mathbf{p}) - \mathbf{F}^- (\mathbf{k})) \end{array} \right] \mathbf{M}^{k_1} (\mathbf{P}, \omega) = I + \int \frac{d^3 \mathbf{k}_{2}}{(2\pi)^3} \left| \mathbf{k}, \mathbf{k}_2 (\mathbf{P}) \right| \mathbf{M}^{k_2} (\mathbf{P}, \omega)
$$

\[ \text{(A.54)} \]

in the dyad vector space.

Above the effect of the collision interaction is treated in first Born approximation. In general a gas particle may collide virtually an arbitrary number of times. That is, the amplitude associated with the first graph of Fig. 18 must then be replaced by the complete series. This amplitude is obtained from the solution of:

$$
\langle \mathbf{k}', \mathbf{p} | \mathbf{M} (\mathbf{q} + \mathbf{f}) | \mathbf{k}, \mathbf{p} \rangle = \langle \mathbf{k}', \mathbf{p} | \mathbf{\mathbf{\alpha}} \mathbf{\mathbf{\alpha}} | \mathbf{k}, \mathbf{p} \rangle - \sum_{\mathbf{k}_0, \mathbf{p}_1} \langle \mathbf{k}', \mathbf{p} | \mathbf{\mathbf{\alpha}} \mathbf{\mathbf{\alpha}} | \mathbf{k}_0, \mathbf{p}_1 \rangle \delta \sum_{\omega_{n_i}} G^{(1)} (\omega_{n_i}, \mathbf{\mathbf{\alpha}}, \mathbf{\mathbf{\alpha}}) \quad \text{\[ (A.55) \]}
$$

Upon carrying out the frequency sum
\[ \mathcal{J}^T(\phi + \xi) = \mathcal{V} + \mathcal{V} \left[ \phi + \xi \pm i e^{-K_0^a - K_0^p + \mu_a + \mu_p} \right]^{-1} (1 - n_a)(1 - n_p) \times \left( 1 - e^{-\rho(K_0^a - \mu_a)} e^{-\rho(K_0^p - \mu_p)} \right) \mathcal{J}^T(\phi + \xi) \] (A.56)

where \( \alpha^+ \phi + \xi \) denotes the two branches of \( M(\phi + \xi + i\epsilon) \).

In the limit of low atom density and Boltzmann statistics for the gas:

\[ e^{-\rho(K_0^a - \mu_a)} \to 0 \]
\[ 1 - n_a \to 0 \]
\[ 1 - n_p \to 0 \] (A.57)

\[ \mathcal{J}^T(\phi + \xi) = \mathcal{V} + \mathcal{V} \left[ \phi + \xi \pm i e^{-K_0^a - K_0^p} \right]^{-1} \mathcal{J}^T(\phi + \xi) \] (A.58)

(A.58) is precisely the two-particle scattering operator where the chemical potentials have been absorbed into \( \phi + \xi \). The collision kernel now becomes:

\[ K_{\alpha', \alpha}^{K_1, K_2}(P) = i \int \frac{d^2p_1}{(2\pi)^3} \frac{d^2p_2}{(2\pi)^3} n(p_1) \sum_{\sigma_1} \left( \frac{\epsilon_{\sigma_1}(K_2) + \epsilon(p_2) - \epsilon_{\beta}(K_1) - \epsilon(p_1)}{\epsilon_{\sigma_1}(K_2) + \epsilon(p_2) - \epsilon_{\beta}(K_1) - \epsilon(p_1)} \right) \]
\[ \times \langle \sigma_1 \beta' | T^- (K_2, p_2) T^+ (P + K_1, p_1) T (P + K_1, p_1) T (P + K_2, p_2) \rangle \] (A.59)
with

$$\langle k', r' | T^\dagger_{k, r} | k, r \rangle = \delta(k + r' - k - r) T^\dagger_{k, r} | k', r' \rangle \quad \text{(A.60)}$$
\[ \langle k', \alpha', p' | M(\phi + \xi) | k, \alpha, p \rangle = \]

\[ \begin{array}{c}
\text{Fig. 18}
\end{array} \]
APPENDIX B. Reduced Diagrams and Rules
for Calculating Absorptive Parts

In the following discussion skeleton diagrams will be used. That is, all diagrams have self-energy insertions removed, and each line has associated with it an exact single-particle propagator. The discussion is equally valid for any given order of perturbation theory where free propagators are used throughout. The system is composed of photons and Fermions.

For Fermion lines

\[ G_z(\omega_n) = \int_{-\infty}^{\infty} d\phi \frac{A_z(\phi)}{\omega_n - \phi} \]  \hspace{1cm} (B.1)

and for the photon lines

\[ D_x(\omega_m) = \int_{-\infty}^{\infty} d\phi \frac{A_x(\phi)}{\omega_m - \phi} \]  \hspace{1cm} (B.2)

Here \( z,x \) are line labelings, i.e., particle type, internal state, momentum, etc.

An arbitrary diagram contributing to \( \phi(\omega_n, \omega_m) \) may be written:

\[
\Phi^{(p)}(\omega_n, \omega_m) = \sum_{z,x} g^{(p)}(z,x) \int_{-\infty}^{\infty} d\phi \frac{A_z(\phi)}{\omega_n - \phi} \ldots \int_{-\infty}^{\infty} d\phi \frac{A_x(\phi)}{\omega_m - \phi} \sum_{\omega_{n_i} \ldots \omega_{n_k}} \sum_{\omega_{m_i} \ldots \omega_{m_l}} \left[ \ldots \right]^{-1} \]  \hspace{1cm} (B.3)

\[ \times \left[ \ldots \right]^{-1} \]
where \( p \) indicates a particular diagram with \( r \) Fermion lines, \( s \) boson lines, and \( u + t \) independent \( \omega \)'s. \( \sum_{z,x} \) denotes various line-labeling sums with \( g^{(p)}(z,x) \) representing all the matrix elements, sign factors, etc., and the \( \Omega \)'s are linear combinations of the \( \omega \)'s.

If the \( \omega_n \) sums are performed energy denominators linear in the \( \omega_n \) appear. Upon analytically continuing \( \omega_n \rightarrow \omega \), one finds that these denominators give poles as \( \omega \) approaches the real axis. To locate the positions of these poles, J.S. Langer noted that the same energy denominators appear in the finite-temperature theory as in the zero-temperature theory.\(^9\) This fact is convenient since Landau's reduced graph procedure may be used in the zero-temperature limit. Under the limit

\[
\beta \rightarrow \infty \quad \frac{1}{\beta} \sum_{n \rightarrow \infty} \frac{1}{n} \int d\omega
\]

the frequency sums may be written:

\[
I(\omega_{\phi_1}, \ldots, \omega_{\phi_s}) = \int_{-i\infty}^{i\infty} \int_{-i\infty}^{i\infty} \int_{-i\infty}^{i\infty} \int_{-i\infty}^{i\infty} \int_{-i\infty}^{i\infty} \frac{1}{(\omega_{\phi_1} - \frac{\pi}{\beta} \cdots \omega_{\phi_s} - \frac{\pi}{\beta})}
\]

where for notational convenience let

\[
\phi_1 = \phi_{n+1}, \ldots, \phi_r = \phi_{r+s}
\]
In the usual manner rationalize with

\[ \prod_{i=1}^{L} (x_i + \alpha_i) \]

and introduce the Feynman parametrization. Equation (B.3) becomes:

\[
\mathcal{I}(w_1, \ldots) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \prod_{i=1}^{L} (x_i + \alpha_i) \delta(\sum_{i} x_i - D) \, D \]

where

\[
D = \sum_{i=1}^{L} \alpha_i (x_i^2 - \alpha_i^2).
\]

An integral transform in a single variable becomes singular when a singularity of the integrand coincides with an endpoint of the integration contour or when the contour is "pinched" by two singularities of the integrand which straddle the contour and develop a coincident singularity on the contour. Analogously, Eq. (B.4) may be regarded as a multiple integral transform and develops singularities for vanishing D such that either:

1. an endpoint singularity or
2. a pinch singularity
appears in every stage of integration. Thus singularities occur for $D = 0$, and either $\alpha_i = 0$ (endpoint) or

$$\frac{\partial D}{\partial w_i} = 0, \quad \frac{\partial D}{\partial \kappa_i} = 0$$

(pinches). These conditions yield the Landau line and loop equations:

1. $\alpha_i = 0$ or $\xi_i - \Omega_i = 0$

2. $\alpha_i(t) \xi_i = 0$ for each closed loop in the graph.

I develops a singularity in $\omega$ when this set of equations yields a determined solution. A purely algebraic procedure would be to start with all $\alpha_i = 0$ and set as many $\alpha_i = 0$ until a determined set of equations is obtained. Then those lines for which $\alpha_i = 0$ are excluded from consideration, and the vertices connected by these lines may be fused together. Thus one obtains the reduced graph, the lines of which satisfying

$$\sum_i \beta_i - \lambda_i = 0.$$  \hspace{1cm} (B.6)

An alternative approach is possible. Given a total rate diagram, draw in an auxiliary line such that the graph falls into two connected pieces each one including an external vertex. This procedure is facilitated through the use of auxiliary graphs. An auxiliary graph is obtained by deleting each interaction line and fusing the vertices joined by them. To illustrate the procedure see Fig. 19a., 19b. The value of introducing the auxiliary graph is not apparent in the example shown in Fig. 19a. The somewhat
Fig. 19
more complicated example of Fig. 19b. would be quite difficult
to analyze without the aid of the auxiliary graph.

In the zero-temperature case the analytic properties of
\(\mathcal{g}(\omega, p)\) are used to obtain its discontinuity from a given reduced
graph. At finite temperature no such method exists; if in
\(\mathcal{g}(\omega_n, p)\) one sets \(\omega_n = \omega\) before performing the indicated summations
an essential singularity develops at infinity. Langer constructs
an iteration procedure closely related to the analytic continuation
method for zero temperature. Here a simpler yet heuristic
derivation will be presented.

Consider the reduced diagram of Fig. 20, corresponding to
a particular pole as per the Landau prescription. The reduced
graph is composed of \(c\) Fermion lines and \(d\) photon lines. The
special labeling of lines is possible since the number of independent
frequencies in a reduced graph is equal to the number of lines
with one frequency conservation constraint. The sums in Eq. (B.3)
may be written:

\[
\frac{1}{\rho} \sum_{w_{m_i}} \sum_{w_{m_k}} \cdots = \frac{1}{\rho^{c+d}} \sum_{w_{m_i}} \sum_{w_{m_k}} \cdots
\]

\[
I_{c,d}^{(p)}(w_{m_i}, \ldots, w_{m_c}, \ldots, w_{m_d}, \phi_{\rho+c+1}, \ldots, \phi_{\rho}, \phi_{\rho+1}, \ldots, \phi_{\rho+c}, w_k) \tag{B.7}
\]

\[
x[(w_{m_i} - \phi_{\rho}) \cdots (w_{m_c} - \phi_{\rho+c})(w_{m_k} - \phi_{\rho}) \cdots (w_{m_d} - \phi_{\rho+d})(\rho_d - \phi_d)]^{-1}
\]
Fig. 20
where $I_{c,d}$ is an analytic function of the frequencies $\omega_1, \ldots, \omega_{n_{2c}}$.

The frequency sums may be represented by contour integrals in the usual manner. The iterative procedure of Langer indicates that in the neighborhood of a Landau singularity $I_{c,d}$ may be factored past the integrals evaluated at the singularity. Thus in the neighborhood of a Landau singularity Eq. (B.7) becomes:

$$
\sum_{\omega_{n_1}} \sum_{\omega_{n_{2c}}} \left[ (\omega_{n_{1}} - \phi_{1}) \cdots (\omega_{n_{2c}} - \phi_{1}) \right]^{-1} \left[ (\omega_{n_{1}} - \phi_{2}) \cdots (\omega_{n_{2c}} - \phi_{2}) \right]^{-1} \cdots \left[ (\omega_{n_{1}} - \phi_{d}) \cdots (\omega_{n_{2c}} - \phi_{d}) \right]^{-1} (B.8)
$$

where $I_{c,d}$ has been evaluated for energies given by the Landau equations. Energy conservation across the diagram requires

$$
(\omega_{n_{1}} + \omega_{n_{1} + 1} + \cdots + \omega_{n_{2c}} - \omega_{n_{2c} + 1} - \cdots - \omega_{n_{2c} + 1}) (B.9)
$$

Write

$$
\frac{\tau_d}{\phi_d} = \sum_{\omega_{md}} \delta_{\omega_{md}, \omega_{md}} \frac{1}{\omega_{md} - \phi_d} (B.10)
$$

with

$$
\delta_{\omega_{md}, \omega_{md}} = \rho \int e^{-t(\omega_d - \omega_{md})} \, dt (B.11)
$$
The remaining energy sum may be written:

\[
\int_0^\infty e^{\sum n_t} dt \left[ \frac{1}{\beta} \sum e^{\sum w_{n_t}} (\omega_n - \beta) \right] \left[ \sum e^{\sum w_{n_e}} (\omega_n - \beta) \right] \\
\times \left[ \frac{1}{\beta} \sum e^{\sum w_{n_\ell}} (\omega_n - \beta) \right] \\
\left[ \sum e^{\sum w_{n_\ell}} (\omega_n - \beta) \right]
\]

...(B.12)

and hence these sums may be performed independently of each other.

For Fermions,

\[
\frac{1}{\beta} \sum e^{\sum w_{n_t}} = \int f_t(\beta) e^{\beta t}
\]

...(B.13)

\[
\frac{1}{\beta} \sum e^{\sum w_{n_s}} = - (1 - f_t(\beta)) e^{\beta t}
\]

...(B.14)

and for photons,

\[
\frac{1}{\beta} \sum e^{\sum w_{n_\ell}} = -(1 + f_\ell(\beta)) e^{\beta_t}
\]

...(B.15)

where

\[
f_t(\beta) = \left[ e^{\beta t} \right]^{-1}
\]

...(B.16)
Then Eq. (B.12) may be written:

\[
(-1)^d (-1)^e \prod_{i=1}^{2c} f_i (\xi_i) \prod_{i=C+1}^{d} (1 - f_i (\xi_i)) \prod_{i=1}^{2c} (1 + f_i (\phi_i)) 
\]

\[
\times \exp (-\sum_{i=1}^{c} \xi_i + \sum_{i=C+1}^{2c} \xi_i + \sum_{i=1}^{d} \phi_i) 
\]

\[
x \left[ \omega - (\sum_{i=1}^{c} \xi_i + \sum_{i=C+1}^{2c} \xi_i + \sum_{i=1}^{d} \phi_i) \right]^{-1}
\]

where the integration has been performed. Comparing with the spectral representation on page 12, one finds the particular reduced graph chosen above contributes to the spectral function the factor,

\[
(-1)^d (-1)^e \prod_{i=1}^{2c} f_i (\xi_i) \prod_{i=C+1}^{d} (1 - f_i (\xi_i)) \prod_{i=1}^{2c} (1 + f_i (\phi_i)) 
\]

\[
\times \exp \left( \omega + \sum_{i=1}^{c} \xi_i - \sum_{i=C+1}^{2c} \xi_i - \sum_{i=1}^{d} \phi_i \right)
\]

If one limits the integrations of the spectral representations for the photons to \( \phi > 0 \), then (B.18) becomes:

\[
(-1)^d (-1)^e \prod_{i=1}^{2c} f_i (\xi_i) \prod_{i=C+1}^{d} (1 - f_i (\xi_i)) \prod_{i=1}^{2c} (1 + f_i (\phi_i)) 
\]

\[
\times \exp \left( \omega + \sum_{i=1}^{c} \xi_i + \sum_{i=C+1}^{d} \phi_i - \sum_{i=1}^{2c} \xi_i - \sum_{i=1}^{d} \phi_i \right)
\]

(B.19)

It is convenient to interpret this factor as corresponding to

(d - b) absorbed photons and c Fermions in the initial state.
and $b$ emitted photons and $c$ Fermions in the final state. For this purpose write:

$$E_i = \sum_{i=1}^{c} \gamma_i + \sum_{i=b+1}^{d} \phi_i$$

$$P_i = \sum_{i=1}^{c} k_i + \sum_{i=b+1}^{d} p_i$$

(B.20)

$$E_f = \sum_{i=c+1}^{c+b} \gamma_i + \sum_{i=1}^{d} \phi_i$$

$$P_f = \sum_{i=c+1}^{c+b} k_i + \sum_{i=1}^{d} p_i$$

(B.21)

The contribution to the absorption rate from a particular reduced diagram may be written:

$$\sum_{\xi_i, \xi_f} S(\xi_i, \xi_f) \mathcal{A}^{(p)}(\omega, P, E_i, E_f)$$

$$\times \delta(\omega_i - E_i \chi_{\ell} \gamma_i) \delta(\omega_f - E_f \chi_{\ell} \gamma_f)$$

(B.22)

where $\xi_i, \xi_f$ collectively represent initial and final state labels and $\sum_{\xi_i, \xi_f}$ the various sums and integrals over these labels. The statistical factor $S(\xi_i, \xi_f)$ is defined:

$$S(\xi_i, \xi_f) = \prod_{i=1}^{c} \frac{1}{1 + f(\xi_i)} \prod_{i=b+1}^{d} (1 - f(\xi_i)) \prod_{i=c+1}^{c+b} f(\xi_i)$$

(B.23)

and

$$\mathcal{A}^{(p)}(\omega, P, E_i, E_f) = \mathcal{E}(E_i, E_f) \mathcal{A}_{i}^{(p)} E_{f}^{(p)}$$

(B.24)
where $Z$ represents the product of the spectral functions associated with each line of the reduced graph, and $A_1(p)$, $E_2(p)$ correspond to the two shaded circles of the reduced graph, i.e., the vertex functions for external photon absorption and emission, respectively. It is useful to write the emission vertex in terms of the corresponding absorption amplitude.

$$E_2(p) = A_2(p)^*$$

Finally, if one sums over all possible vertex amplitudes, that is, all possible diagrams with the same reduced graph, the total contribution to the absorption rate may be written:

$$
\sum_{E_i,E_f} S(E_i,E_f) Z(E_i,E_f) A_1(\omega^+P,E_i,E_f) A_2^*(\omega^+P,E_i,E_f)
\times 2\pi\delta(\omega + E_i - E_f) \delta(\omega + P - P_f)
$$

$$
\sum_{i} A_i(\omega^+P,E_i,E_f) = \sum_i A_i(\omega^+P,E_i,E_f)
$$

Note that the factor $(-1)^c$ in the original statistical factor accounts for the fact that $c$ Fermion loops have been removed from the original diagram. Similarly $(-1)^d$ accounts for the fact that $d$ photon lines have been cut. Thus the overall sign
assignment is made on the basis of the lines internal to the vertex amplitudes.
APPENDIX C. Self-Energy Functions

A self-energy graph is obtained by removing the free propagation amplitudes from the first and last vertex of a given interacting one-particle propagator amplitude. In general, these graphs are non-diagonal in the internal state of an atom, but they are labeled by a single momentum and frequency. A proper self-energy graph is one which cannot be broken into two connected parts by cutting a single atom line.

It is sometimes useful to consider a more expanded definition of self-energy graphs. For example one might speak of $\alpha$-proper self-energy graphs, i.e., all possible self-energy diagrams which cannot be broken into two connected graphs simply by cutting a line labeled by $\alpha$. More generally it is possible to speak of $\beta$-proper self-energy graphs where no single line from the $\beta$ collection appears in the graph. In this case the matrix element of $G$ in the space of internal states satisfies:

$$
\langle \alpha | G | \alpha' \rangle = \langle \alpha | \alpha' \rangle \langle \alpha | G_0 | \alpha' \rangle + \langle \alpha | G_0 | \alpha' \rangle \sum_{\beta \gamma} \langle \beta | \phi_\beta | \alpha' \rangle \langle \alpha' | G_0 | \alpha' \rangle \\
+ \langle \alpha | G_0 | \alpha' \rangle \langle \alpha' | \phi_\beta | \alpha' \rangle \langle \alpha' | G_0 | \alpha' \rangle
$$

(c.1)

where $\varnothing_{\beta}$ represents all those self-energy graphs which are "$\beta$-proper."
Equation (C.2) may be solved for \( G_{\alpha\alpha'} \).
\[
\langle \alpha | G (\omega_n P) | \alpha' \rangle = \left( \omega_n + \mu_n - \varepsilon_{\alpha}(k) - \langle \alpha | \Phi_n | \alpha \rangle \right)^{-1}
\]
\[
\times \left( \langle \alpha | \alpha' \rangle + \sum_{\alpha_g} (1 - \langle \alpha_g | \alpha \rangle) \langle \alpha | \Phi_n | \alpha_g \rangle \langle \alpha_g | G | \alpha' \rangle 
+ (1 - \sum_{\alpha_g} \langle \alpha_g | \alpha' \rangle) \langle \alpha | \Phi_n | \alpha' \rangle \langle \alpha' | G | \alpha' \rangle \right) \tag{C.3}
\]

In special cases this result simplifies.

With

1. \( \Phi = \) a single state

\[
\langle \alpha | G | \alpha' \rangle = \left( \omega_n + \mu_n - \varepsilon_{\alpha}(k) - \langle \alpha | \Phi_n | \alpha \rangle \right)^{-1}, \tag{C.4}
\]

and

\[
\langle \alpha | G | \alpha' \rangle = \left( \omega_n + \mu_n - \varepsilon_{\alpha}(k) - \langle \alpha | \Phi_n | \alpha \rangle \right)^{-1} 
\times \langle \alpha | \Phi_n | \alpha \rangle \left( \omega_n + \mu_n - \varepsilon_{\alpha}(k) \right)^{-1} ; \tag{C.5}
\]
2. $\mathfrak{S} = \text{the whole spectrum}$

$$
\langle \alpha | G | \alpha \rangle = \left( \omega_n + \mu \kappa - \epsilon_k - \langle \alpha | \Phi | \alpha \rangle \right)^{-1} \\
\times \left( 1 + \sum_{\alpha'' \neq \alpha} \langle \alpha | \Phi | \alpha'' \rangle \langle \alpha'' | G | \alpha \rangle \right), \tag{c.6}
$$

and

$$
\langle \alpha | G | \alpha \rangle = \left( \omega_n + \mu \kappa - \epsilon_k - \langle \alpha | \Phi | \alpha \rangle \right)^{-1} \\
\times \left[ \langle \alpha | \Phi | \alpha \rangle \langle \alpha | G | \alpha \rangle + \sum_{\alpha'' \neq \alpha} \langle \alpha | \Phi | \alpha'' \rangle \langle \alpha'' | G | \alpha \rangle \right]. \tag{c.7}
$$

3. $\mathfrak{S} = \text{states degenerate with } \alpha \ (\text{useful for broadening calculations}).$ For $\alpha' \in \mathfrak{S}$

$$
\langle \alpha' | G | \alpha \rangle = \left( \omega_n + \mu \kappa - \epsilon_k - \langle \alpha' | \Phi | \alpha \rangle \right)^{-1} \\
\times \left[ 1 + \sum_{\alpha_{ij} \neq \alpha} \langle \alpha' | \Phi | \alpha_{ij} \rangle \langle \alpha_{ij} | G | \alpha \rangle \right], \tag{c.8}
$$

and

$$
\langle \alpha' | G | \alpha \rangle = \left( \omega_n + \mu \kappa - \epsilon_k - \langle \alpha' | \Phi | \alpha \rangle \right)^{-1} \\
\times \sum_{\alpha_{ij} \neq \alpha} \langle \alpha' | \Phi | \alpha_{ij} \rangle \langle \alpha_{ij} | G | \alpha \rangle \tag{c.9}
$$

Other choices are possible depending on the specific situation.
Case 1. is equivalent to the perturbation expansion of Heitler in his treatment of resonance fluorescence for atoms in a vacuum. 2. is the usual definition of the self-energy function. Such a perturbation scheme was used by F. Low in a calculation of the natural line shape. 3. may be useful where the particular level of interest is degenerate and off-diagonal elements within this degenerate collection of states is desired.
APPENDIX D. Symmetry Properties of the One-Particle Propagator

The one-particle atom propagator enjoys certain selection rules upon considering the group of symmetry transformations $T$ of the full Hamiltonian $H$.

The explicit expression for the one-particle atom propagator in configuration space is written:

$$G_{\kappa\kappa'}(X_i-X_{i'})\rho_{\gamma}\rho_{\gamma'}=-\text{Tr}\left[e^{i\int_{t_0}^{t_f}(H_{\kappa\kappa'}-N-H)}T_{\kappa\kappa'}(X_i,\rho_{\gamma})T_{\kappa\kappa'}(X_{i'},\rho_{\gamma'})\right]$$

(D.4)

Here

$$\psi(X,\rho)=e^{i(H-\mu\cdot N)\rho/\hbar}\psi(X,0)e^{-i(H-\mu\cdot N)\rho/\hbar}$$

(D.5)

and $\psi(X,0)$ creates an atom with c.m. position $X$ in an internal state $\gamma$.

Restrict $T$ here to include all transformations induced by a rotation of the observer's coordinate frame about a direction $\hat{n}$ by an angle $\theta$. Thus,

$$X_i' = \sum' R_{i'p}(\theta,\hat{n})X_i$$

(D.6)
where the $X'_{ij}$ are the coordinates in the new frame of a vector whose coordinates in the original frame are $X_j$. Equivalently, one may consider the system as rotated by an angle $\theta$ about $\hat{n}$.

For such a rotated system the field operators become:

$$O_{R'} \Psi_{\alpha'} (X_{ij}, \beta_i) O_R^{-1} = \sum_{\gamma} \Psi_{\gamma} (R^{-1} X_{ij}, \beta_i) D_{\alpha' \gamma} (R^{-1})$$  \hspace{1cm} (D.7)

$$O_{R'} \Psi_{\alpha'} (X_{ij}, \beta_i) O_R^{-1} = \sum_{\gamma} \Psi_{\gamma}^* (R^{-1} X_{ij}, \beta_i) D^{*\alpha' \gamma} (R^{-1})$$  \hspace{1cm} (D.8)

The $D$'s are matrix elements of the irreducible representations of the rotation group and thus are indexed by a total angular momentum quantum number $J_\alpha$ and angular momentum projections $M_J$. These explicit dependences will be shown when convenient.

The right side of Eq. (D.4) may be written:

$$-T_{\alpha'} \left[ e^{\theta (\hat{n} \cdot \mathbf{p} + \mathbf{N} - H)} T_{\gamma} \Psi_{\alpha'} (X_{ij}, \beta_i) \Psi_{\gamma}^* (X_{ij}, \beta_i) O_R^{-1} O_R \right]$$

$$= -T_{\alpha'} \left[ e^{\theta (\hat{n} \cdot \mathbf{p} + \mathbf{N} - H)} T_{\gamma} O_R \Psi_{\alpha'} (X_{ij}, \beta_i) O_R^{-1} O_R \Psi_{\gamma}^* (X_{ij}, \beta_i) O_R \right]$$

$$= \sum_{\gamma} D_{\gamma \gamma'} \left( R^{-1} \right) D^{*\gamma' \gamma} \left( R^{-1} \right) \left[ -T_{\alpha'} \left[ e^{\theta (\hat{n} \cdot \mathbf{p} + \mathbf{N} - H)} T_{\gamma} \Psi_{\gamma}^* (X_{ij}, \beta_i) \Psi_{\alpha'} (X_{ij}, \beta_i) \right] \right]$$  \hspace{1cm} (D.9)

where use has been made of $[H, O_R] = [N, O_R] = 0$, cyclic invariance of the trace, and Eqs. (D.7) and (D.8). But the bracketed expression is again a one-particle propagator. Thus
\[ G_{\alpha \beta}(X_1 - X_2, \beta - \beta_2) = \sum_{\gamma, \gamma'} G_{\gamma \gamma'} (R^{-1}(X_1 - X_2), \beta - \beta_2) D_{\gamma \gamma'}^* (R^{-1}) D_{\gamma' \gamma} (R^{-1}) \]  

(D.10)

or

\[ \int \frac{d^3 k}{(2\pi)^3} e^{-i k \cdot (X_1 - X_2)} G_{\alpha \beta}(k, \beta - \beta_2) \]

\[ = \sum_{\gamma, \gamma'} \int \frac{d^3 k}{(2\pi)^3} e^{-i k' \cdot R^{-1}(X_1 - X_2)} G_{\gamma \gamma'}(k', \beta - \beta_2) D_{\gamma \gamma'}^* (R^{-1}) D_{\gamma' \gamma} (R^{-1}) \]  

(D.11)

Set \( k' = R^{-1} k \) on the right hand side of Eq. (D.11). Then Eq. (D.11) becomes:

\[ \sum_{\gamma', \gamma} \int \frac{d^3 k}{(2\pi)^3} G_{\gamma' \gamma}(R^{-1} k, \beta - \beta_2) e^{-i k \cdot (X_1 - X_2)} D_{\gamma' \gamma}^* (R^{-1}) D_{\gamma \gamma} (R^{-1}) \]  

(D.12)

Thus,
where a Fourier series decomposition in $(\beta_1 - \beta_2)$ has been used. It is convenient to write $\alpha = (J M Z)$, exhibiting angular momentum numbers explicitly; $Z$ denotes all additional quantum numbers necessary to fully specify the state. Then

$$G_{\alpha \alpha} (\kappa, \omega) = \sum_{\gamma, \gamma'} G_{\gamma \gamma} (R' \kappa, \omega) D_{\alpha \gamma}^* (R^{-1}) D_{\alpha' \gamma'} (R^{-1})$$

(D.13)

It is impossible to proceed further without making some simplifying assumptions regarding the effects of collisions is spherically symmetric. Anderson and Baranger have discussed the results of this assumption in their theories of pressure broadening. Here this assumption takes the following form:

$$G_{J M Z} (R' \kappa, \omega) = \sum_{J' M' Z'} \frac{G_{J' M' Z'}}{J' M' Z'}$$

(D.14)

It is not sufficient merely to assume that the gas is isotropic, for an atom with a non-zero angular momentum defines a preferred direction. Equation (D.15) follows trivially if spin-orbit
interactions are absent since in this case the Hamiltonian is invariant under separate rotations of the c.m. coordinates and the internal coordinates of the atom.

With Eq. (D.15) integration of both sides of (D.14) over all possible rotations yields:

\[
\frac{C (k, \omega_n)}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \int dR = \sum_{M_{x}, M_{y}, M_{z}} \frac{G (k, \omega_n)}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \int dR
\]

\[
\times \int D^{(T_{\omega_n})}_{M_{x}, M_{y}} (R^{-1}) D^{(T_{\omega_n})}_{M_{x}, M_{y}} (R^{-1}) dR
\]

\[
= \sum_{M_y, M_{y'}} \frac{\delta_{M_{y}, M_{y'}}}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \frac{\delta_{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}}}{2J_{\omega_n} + 1} \frac{G (k, \omega_n)}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \int dR
\]

where the orthogonality relationship for the representation coefficients has been used. But this result means that

\[
\frac{C (k, \omega_n)}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \int dR = \sum_{M_y, M_{y'}} \frac{\delta_{M_{y}, M_{y'}}}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \frac{\delta_{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}}}{2J_{\omega_n} + 1} \frac{G (k, \omega_n)}{J_{\omega_n} M_{\omega_n} \hat{Z}_{\alpha}} \int dR
\]
FOOTNOTES AND REFERENCES


FIGURE CAPTIONS

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Fig. 11. Collision broadening (lower level unperturbed).

Fig. 12. Renormalized atom propagator (radiative corrections).

Fig. 13. Reduced graph expansion of Fig. 11a. (one photon emission).

Fig. 14. Reduced graphs with renormalized propagators
   a. Pure photon emission.
   b. Pure collision.
   c. Collision and photon emission.

Fig. 15. \( \Gamma_f^{(0)} \)

Fig. 16. Open diagrams for quenching and fluorescence.

Fig. 17. Contours for frequency sums.

Fig. 18. Born series expansion in gas-atom collisions.

Fig. 19. Examples of reduced graphs procedure.

Fig. 20. Arbitrary reduced graph.
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