THE UNIVERSITY OF MICHIGAN
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SCATTERING OF LIGHT FROM ATOMS, MOLECULES AND FREE ELECTRONS IN GASES AND PLASMAS

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ABSTRACT

In this dissertation some basic relationships concerning the scattering of light from particles which are very small compared to wavelengths of interest—specifically free electrons, ions, atoms and simple molecules—are examined from a consistent application of quantum perturbation theory to a many body system. Of major concern are particles in gaseous or plasma systems, although many of the results may have broader validity. For the most part attention is confined to nonresonance, linear, single scattering. Higher ordered corrections to the scattering cross section which arise from the variation of the refractive index from unity are neglected and the possible effects of variations in the intensity of incident radiation over distances comparable to wavelengths of interest are not considered in detail. The results obtained under these conditions appear to retain wide limits of applicability which are discussed in Chapter I. However, where necessary, all of these conditions can be relaxed to varying degrees through procedures which are mentioned at appropriate points in Chapter I.

Among the major results obtained here are, first, a consistent and informative derivation of the dependence of light scattering in gases on particle-particle interactions; second, a comparitively simple derivation of the angular distribution of the scattered light; third, detailed relationships between scattering cross sections and oscillator strengths which permit the calculation of Rayleigh and Raman scattering cross sections under appropriate conditions; and fourth, a relationship between familiar quantum expressions for scattering cross sections and refractive indices which is significantly different than the well known classical relationship under conditions for which the classical relationship is often assumed to be valid.

INTRODUCTION

In the late 1800's light scattering began to receive fairly widespread attention which has persisted to the present and is now being enhanced by the recent and continuing development of intense monochromatic light sources and sensitive detection schemes. As evidence of this attention, many thousands of articles and books directly concerned with light scattering have appeared since 1800. In the following paragraphs an attempt is made to summarize the major published results up to August, 1965, which pertain most directly to this dissertation. After the summary, the dissertation is outlined and the results which appear to be significant are described in some detail.

Recorded observations of light scattering from small particles date back at least to 1802, when Richter[1] observed the path of a light beam passing through a sol of colloidal gold. Tyndall[2] reinvestigated this effect in clouds of small particles created by chemical interactions between vapors. He observed (1869) that the scattered light is predominantly blue, and if the incident light is polarized, the scattering is then visible only in the plane perpendicular to this polarization.

While Tyndall and many others thought that scattering from similar particles might account for the blue color of the sky, Lord Rayleigh[3] argued that this phenomenon arises primarily from scattering by molecules. In establishing this point of view, Rayleigh[4] developed (1899) a theory

of light scattering from molecules based on Maxwell's equations and the idea that the oscillating electric field representing a beam of incident radiation induces oscillating dipoles in scattering particles. These oscillating dipoles set up a secondary radiation field which represents the scattered radiation. In general the radiation scattered from different particles interferes such that the total effect may depend sensitively on the relative positions of particles. However, Rayleigh[4,5] showed that if the interactions between particles are neglected (ideal gas assumption) then the effects of interference vanish and the total intensity of scattered radiation may be obtained by calculating the intensity of light scattered by a single characteristic particle and then multiplying by the number of scattering particles.

In 1915 Cabannes[6] reported the first observation of light scattered from carefully filtered gas. Shortly thereafter, Smoluchowski[7] and Strutt[8] (Lord Rayleigh's son) confirmed this observation in independent experiments. Rayleigh's theory successfully explained the gross features of the scattering; e.g., the preponderance of blue scattering and the (approximate) relationship between the scattering cross section and corresponding refractive indices. Although in its earliest form this theory predicted that the light scattered through 90° would be totally polarized perpendicular to the plane of scattering, Strutt[9] (1918) and others observed slight depolarization in the light so scattered. Through a modification of his theory, introducing the assumption of anisotropic

scattering particles, Rayleigh[10] was able to explain the presence of depolarization and to relate it to the structure of the scattering particles.

Rayleigh's classical theory, suitably modified, has been employed extensively up to the present time. Its popularity arises at least in part from the simplicity and familiarity of its concepts and the fact that its predictions have been reasonably consistent with the experimental data obtained to date.

This theory does not apply directly to scattering of light from particles whose linear dimensions are comparable to the wavelength of the incident radiation or to systems of particles whose mutual interactions observably effect the scattering. For the first case Rayleigh[11] and Gans[12] developed extensions to Rayleigh's basic theory for particles of intermediate size, and Mie[13] (1908) developed a general theory.

With reference to the second case, the interactions between simple molecules or atoms in gaseous systems away from a critical point appear to affect the scattering directly only in fine detail. Experimental observations of this fine detail have not been reported yet, but it appears likely that these experiments are becoming feasible. However, near a critical point in gases, and in plasmas, liquids and solids, particle-particle interactions play an important role in determining light scattering properties.[14]

Two different but equivalent techniques have developed for analyzing the effects of particle-particle interactions on light scattering. First one may combine the contributions of individual particles, taking into account the relative phases of the electric field oscillations representing these contributions at the point of observation. The relative phases for coherent scattering* depend on particle relative positions which may be described, for example, through the introduction of correlation functions. For example, Debye[15] has applied the individual particle approach to dilute solutions of high polymers which do not interact with each other strongly. Very recently, Pecora[16] has extended this approach in order to examine the detailed spectral distribution of light Rayleigh scattered from a monochromatic beam.

Second, the coherent scattering has been treated as the result of fluctuations in the refractive index of the scattering medium which result from statistical fluctuations in macroscopic properties such as density or concentration. This approach is usually based upon classical macroscopic electromagnetic theory. Smoluchowski[17] (1908) first applied the fluctuation analysis to light scattering, using it to account for the strong scattering from gases and solutions near a critical point. Einstein[18] (1910) developed the general fluctuation theory, and Ornstein and Zernicke[19] developed a detailed theory of critical scattering. Brillouin[20] (1922) predicted that fluctuations associated with standing sound waves should break up the Rayleigh scattering line into a doublet. In the first experimental observation of the frequency dis-

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*See Section 2.1.

tribution of the light scattered by a liquid, Gross[21] (1930) observed a central line in addition to this doublet. In 1934 Landau and Placzek[22] attributed the central line to thermal motions which are unorganized in time.

Following these early works a great number of publications concerning classical light scattering theory and related experiments have appeared. Much of the fundamental work is summarized by Born,[23] and, with reference to scattering by simple molecules and atoms, by Cabannes[24] and Bhagavantam.[14]

Shortly after 1940 Debye[15] began development of the applications of light scattering in chemistry. Stacey[25] presents a fairly recent (1956) account of these applications. The theory and applications of light scattering from small particles is presented along with a comprehensive bibliography by Van de Hulst[26] (1957). The more recent publications Electromagnetic Scattering[27] (1963), and Phonons and Phonon Interactions[28] (1964) contain articles concerning light scattering as related to chemistry, astrophysics, atmospheric physics, and physics of the liquid and solid state.

The quantum theory began with a derivation from the correspondence principle by Kramers and Heisenberg[29] (1925) of an expression for the light scattering from an isolated atom. This result was confirmed by Dirac's[30] later derivation (1927) employing a modern formulation of quantum mechanics. Besides the "elastic" light scattering predicted by Rayleigh's classical theory, the results of Kramers and Heisenberg, and Dirac suggested the possibility of "inelastic" light scattering in which, during a scattering transition, the scattering particle changes state and either absorbs or gives up a discrete amount of energy. This inelastic scattering was first identified by Raman[31] (1928) at a time when it provided important confirmation of the quantum light scattering theory and quantum mechanics in general. The inelastic scattering is often referred to as Raman scattering (or the Raman effect) as opposed to the elastic Rayleigh scattering.

The early work on Raman scattering is summarized by Rocard[32] (1928), Cabannes[24] (1929), Kohlrausch[33] (1931) and Bhagavantam[14] (1940). Although quantum mechanics appears to be required for a detailed examination of Raman scattering, many of these significant early contributions proceed at least in part from classical theory. However, in 1931 Placzek began to publish a series of papers in which he developed and examined the quantum expressions for light scattering in detail, and in particular, applied group theory to obtain relationships between the properties of the scattered radiation and the symmetry characteristics of the scattering particles. This series culminated in a detailed review article[34] (1934) treating the general properties of both Rayleigh and Raman scattering.

After Placzek's work, the quantum theory has been applied extensively to resonance scattering from atoms and molecules. Behringer[35] presents a relatively modern account (1958) of the resonance theory. The quantum theory has also been applied extensively to Raman scattering away from resonance,[34] although classical theory is still used to examine various aspects of Raman scattering. The application of quantum theory to Rayleigh scattering away from resonance seems to be less extensive, aside from Placzek's work, perhaps because of the appeal of the classical approach noted earlier.

Most of the published quantum treatments of light scattering from atoms and molecules concentrate on the scattering from a single particle. The scattering from an aggregate of such particles is determined by introducing appropriate phase factors which depend on particle positions, as in one classical approach. In the sense that the dependence on particle positions is not established directly from the basic quantum formulation such approaches represent inconsistent treatments of the scattering by many particle systems, although they lead to correct results under certain conditions.

Soon after the development of the pulsed ruby laser, Hughes[36] (1962) pointed out that scattering of an intense laser beam by free electrons should be observable in a plasma, and if so, the scattered radiation should contain detailed, spatially resolved information about the plasma. Perhaps because of the great interest in plasma diagnostics, and because of a similar problem which had just appeared concerning the scattering of radar waves in the ionosphere,[37] several detailed theoretical analysis of the light scattering by free electrons in a plasma appeared almost immediately. Notable among these analyses are those of Lamb,[38] (1962) Rosenbluth and Rostoker,[39] (1962) and Dubois and Gilinsky[40] (1963). Shortly thereafter considerations of relativistic effects,[41] collision effects[42] and nonlinear scattering appeared.[43] The first experimental observation of light scattering from a laboratory plasma was reported by Fünfer and coworkers[44] (1963) and, as experimental difficulties were solved, more detailed observations were reported. This technique is being developed into a useful diagnostic tool as evidenced by the numerous reports of plasma light scattering experiments which have been presented recently.[45]

Laser sources also greatly extend the experimental capabilities for light scattering from gases, liquids, and solids. First, the extreme intensity of laser beams renders visible all sorts of interesting nonlinear phenomena. The first observation of such phenomena were reported by Colgrave, Franken, Lewis, and Sands.[46] Terhune and coworkers[47] have also published numerous observations of nonlinear phenomena.

Second, the extreme collimation, coherence, and monochromaticity which is characteristic of laser beams allow the observation of fine detail of the scattered light which contains a great deal of information about the properties of the scattering medium. The theoretical work of

Pecora[16] and the recent experiments reported by Rank, Kiess, Fink, and Wiggens[48] illustrate this remark.

In this dissertation some basic relationships concerning the scattering of light from particles which are very small compared to wavelengths of interest—specifically free electrons, ions, atoms, and simple molecules—are examined from a consistent application of quantum mechanical perturbation theory to a many particle system. Of major concern are particles in gaseous or plasma systems, although many of the results may have broader validity. For the most part attention is confined to non-resonance, linear single scattering. Higher order corrections to the scattering cross section which arise from the variation of the refractive index from unity are neglected and the possible effects of variations in the intensity of incident radiation over distances comparable to wavelengths of interest are not considered in detail. The results obtained under these conditions appear to retain wide limits of applicability which are discussed in Chapter I. However, where necessary, all of these conditions can be relaxed to varying degrees through procedures which are mentioned at appropriate points in the main text.

In Chapter I a general light scattering cross section for free electrons, ions, atoms, and molecules in a gas or plasma is derived. The dependence of the cross section on relative positions of the scattering particles and on the particle internal degrees of freedom are developed consistently. In this development terms arise corresponding to scattering transitions in which two particles simultaneously change state. In Appendix C it is shown that these terms have a very strong resonance behavior and are probably insignificant except perhaps at resonance. Since resonance scattering is not of immediate concern these terms are not considered further.

In Chapter II the dependence of the scattering from a system of particles on the relative positions of the particles is developed through a simple approximation which is valid except within a fraction of an angstrom of resonance. It is shown that this dependence may be expressed in terms of the Van Hove G-functions[49] which are time-dependent correlation functions of particle positions. Similar results have been obtained recently by others from classical[16] and quantum[50] approaches. However, it appears that the present derivation provides considerably more information about the range of validity of this formulation. Also in Chapter II the cross section integrated over final frequency is expressed in terms of simpler correlation functions through the static approximation which is familiar in neutron and x-ray scattering theory. Finally a rough quantitative estimate of the significance of interference effects between different scattering particles in gases is developed. From this estimate it appears that these effects should be negligible in nonresonance light scattering from gases of atoms and simple molecules except in the vicinity of a critical point, insofar as the scattering integrated over final frequency is concerned. This conclusion is already well accepted although the quantitative estimate is perhaps of some interest. However the possible importance of interference in determining the fine detail of the frequency distribution of light scattered from gases is not ruled out.

In Chapter III the scattering from free electrons in a plasma is considered briefly. This chapter does not contain any significant original contributions to the extensive work already published in this field. However, perhaps of some interest is the comparison of the interference of scattering from free electrons with scattering from the other particles which are present in a plasma. In most published analyses of scattering from free electrons in a plasma, it is assumed that the free electron scattering predominates overwhelmingly or at least may be considered separately. The approximation involved in this assumption is displayed explicitly and discussed briefly in Chapter III.

In Section 4.1 the dependence of the scattering from atoms, ions, and molecules on the internal states of these particles is developed into a form which is identical to that obtained previously by, for example, Dirac[51] and Placzek.[34] In Section 4.2 the angular dependence of the scattering is derived using well known selection rules. Although this angular dependence is the same as that obtained from classical theory,[23] and is implied but not put into the most convenient form in Placzek's quantum treatment,[34] the present derivation may be of interest because of its relative simplicity. In Section 4.3 it is shown that various light scattering cross sections may be calculated from appropriate oscillator strengths. The expressions for these calculations are put into a particularly simple form using the Wigner-Eckart theorem. These results extend those of Placzek,[34] who developed only the relationship between the so-called trace scattering and oscillator strengths. Also in Section 4.3 a relationship between Rayleigh scattering cross sections and a well known quantum expression for the refractive index is developed. A potentially significant difference exists between this expression and the usual classical expression. Using the properties of Racah coefficients this difference is expressed in a simple form. In Section 4.4, some of the results of previous sections are illustrated through the calculation of Rayleigh scattering cross sections for ground state cesium atoms from oscillator strengths. The results are interesting for several reasons:

a) The predominant cross section is large, being on the order of or greater than 10^{-25} cm^2 for incident wavelengths from 6000 Å to 10,000 Å, compared to cross sections for most atom and simple molecules which are on the order of 10^{-28} cm^2.

b) The transverse depolarization of the scattered radiation is significant over wide spectral regions away from resonance. This result contradicts the frequent supposition that atoms cannot depolarize transverse scattered radiation because, in some sense, they are spherically symmetric.

c) The quantum relationship between the Rayleigh cross sections for ground state cesium atoms and the corresponding refractive index is in profound disagreement with the classical relationship over spectral regions well removed from resonance, such that for this special case the descrepancy between these two relationships ought to be accessible to conclusive experimental verification.

In Section 4.5 the relationship between the properties of the scattered radiation and the symmetry of the scattering particles is discussed briefly, and it is shown that the symmetry theory does not preclude depolarization of transverse-scattered radiation by particles with spherically symmetric change distributions in initial and final states.

Finally in Chapter V some of the implications of the results of this dissertation are discussed and areas of possibly interesting future work are mentioned.

CHAPTER I

DERIVATION OF A GENERAL LIGHT SCATTERING CROSS SECTION FOR PARTICLES WHICH ARE VERY SMALL COMPARED TO WAVELENGTHS OF INCIDENT AND SCATTERED RADIATION

In Chapter I we present a quantum analysis of light scattering interactions in a gas or plasma. This analysis leads to the development of scattering cross sections which relate the properties of the scattered radiation to those of the incident radiation and scattering system. In the theoretical approach adopted here we consider the scattering interactions which occur in an arbitrarily large cubical cell. This cell procedure has been employed frequently for similar calculations, for example by Heitler,[52] Schiff,[53] and Messiah.[54] In each of their presentations it is required that the cell should be so large that its size does not affect the results of the calculation when one is calculating, for example, a rate per unit volume. We shall also adopt this requirement for the derivation of scattering cross sections to follow. In Section 1.5 it is argued that the large cell procedure should lead to a correct analysis of the scattering at least as long as the properties of the radiation (for example, intensity and spectral distribution) in the actual experiment do not change significantly over distances comparable to wavelengths of interest.

1.1. THE HAMILTONIAN FOR THE SCATTERING SYSTEM

The Hamiltonian for the scattering system within the cell may be written in the form

$$H = \sum_{j} \frac{\left(\underline{p}_j - \frac{e_j}{c}\underline{A}_j\right)^2}{2m_j} + V + H^R \tag{1.1}$$

The sum over j is over all electrons (including bound electrons) and nuclei in the cell. The potential V represents interactions between all of the electrons and nuclei within the cell. H^R is the Hamiltonian for the radiation.

Following a familiar procedure[52] the radiation fields within the cell are Fourier analyzed in terms of functions which, for mathematical convenience, are required to satisfy periodic boundary conditions on the walls of the cell. As a result one obtains

$$H^R = \sum_{\lambda} \hbar c k_\lambda \alpha_\lambda^\dagger \alpha_\lambda \tag{1.2}$$

and

$$\underline{A}_j = \sum_{\lambda} \left(\frac{2\pi\hbar c}{L^3 k}\right)^{1/2} \underline{\epsilon}_\lambda \left[\alpha_\lambda^\dagger e^{-i\underline{k}_\lambda \cdot \underline{r}_j} + \alpha_\lambda e^{i\underline{k}_\lambda \cdot \underline{r}_j}\right] \tag{1.3}$$

Here L is the dimension of the cell. Notice that the subscript j designates the point in space at which $\underline{A}$ is to be evaluated. The index λ indicates a particular photon state of polarization $\underline{\epsilon}_\lambda$ and propogation vector $\underline{k}_\lambda$. The sum over λ implies a sum over all values of $\underline{k}_\lambda$ consistent with the periodic boundary conditions and a sum over two orthogonal polarizations for each value of $\underline{k}_\lambda$. We note that in order to satisfy the boundary condition just introduced $\underline{k}_\lambda$ assumes the values

$$\underline{k}_\lambda = \frac{2\pi \ell_\lambda}{L}\,\underline{e}_x + \frac{2\pi m_\lambda}{L}\,\underline{e}_y + \frac{2\pi n_\lambda}{L}\,\underline{e}_z \tag{1.4}$$

where $\underline{e}_x$, $\underline{e}_y$, and $\underline{e}_z$ are unit orthogonal vectors perpendicular to the cell walls, and ℓ_λ, m_λ, and n_λ assume all integral values in the sum over λ. The polarization vector $\underline{\epsilon}_\lambda$ which along with $\underline{k}_\lambda$ determines a particular photon state is perpendicular to $\underline{k}_\lambda$ such that

$$\underline{\epsilon}_\lambda \cdot \underline{k}_\lambda = 0 \tag{1.5}$$

The expansion coefficients a_λ^+ and a_λ act as photon creation and destruction operators, respectively. (See Eqs. (1.31).)

In this section the Hamiltonian is put into a form which is convenient for the derivation of scattering cross sections. The first step is to separate contributions due to atoms, ions, and molecules (hereafter designated collectively as molecules) from contributions due to free electrons. This separation is introduced by writing the Hamiltonian in the form

$$H = \mathcal{H}^e + \mathcal{H}^M + \mathcal{H}^I + H^R \tag{1.6}$$

where

$$\mathcal{H}^e = \sum_j^{N_e} \frac{\left(\underline{p}_j + \frac{e}{c}\underline{A}_j\right)^2}{2m} \tag{1.7}$$

$$\mathcal{H}^{M} = \sum_{\alpha}^{N_M}\left\{\sum_{j}^{N_\alpha}\frac{\left(\underline{p}_{\alpha j}-\frac{e_j}{c}\underline{A}_{\alpha j}\right)^2}{2m_j} + V_\alpha\right\} = \sum_{\alpha}^{N_M}\mathcal{H}^{M}_{\alpha} \qquad (1.8)$$

Here V_α is the potential representing interactions between the N_α electrons and nuclei in the αth molecule. N_e and N_M are the numbers of free electrons and molecules in the cell. $\mathcal{H}^I$ represents the interactions between particles. (The word "particle" is reserved to designate free electrons and molecules.)

It is convenient to introduce appropriate center-of-mass transformations for the molecules to separate "external" degrees of freedom describing the motion of the center of mass of each molecule from "internal" degrees of freedom describing the motion of bound electrons and nuclei with respect to a molecular center of mass. There are a number of transformations of this type, differing slightly in the definition of transformation variables. A particular type of transformation may be chosen for each type of particle on the basis of convenience. For example, for atoms the transformation defined by

$$\underline{R}_\alpha = \frac{M_{\alpha o}}{M_\alpha}\underline{r}_{\alpha o} + \frac{m}{M_\alpha}\sum_{j}^{Z_\alpha}\underline{r}_{\alpha j} \qquad (1.9)$$

$$\rho_{\alpha j} = \underline{r}_{\alpha j} - \underline{r}_{\alpha o} \qquad (1.10)$$

is convenient. Here $M_{\alpha o}$ and $\underline{r}_{\alpha o}$ are the location and mass of the nucleus; m and $r_{\alpha j}$ are the location and mass of the jth electron in the atom. These transformations are discussed in Appendix A where it is shown that one may write the resulting Hamiltonians in the form

$$\mathcal{H}_{\alpha}^{M} = H_{\alpha}^{MX} + H_{\alpha}^{N} + H_{\alpha}^{MR} \tag{1.11}$$

Here H_{α}^{MX} contains only coordinates associated with the motion of the particle as a whole, H_{α}^{N} contains only coordinates associated with the motions of electrons and nuclei within the particle and H_{α}^{MR} contains those terms which express the interaction between the particle and the radiation field.

It is convenient to write the Hamiltonian for free electrons as given by Eq. (1.7) in the form

$$\mathcal{H}^{e} = H^{e} + H^{eR} \tag{1.12}$$

where

$$H^{e} \equiv \sum_{j}^{N_e} \frac{p_j^2}{2m} \tag{1.13}$$

$$H^{eR} \equiv \sum_{j}^{N_e} \left[\frac{e}{mc} \underline{A}_j \cdot \underline{p}_j + \frac{e^2}{2mc^2} A_j^2 \right] \tag{1.14}$$

The terms H^{MR} and H^{eR} contain the interaction between the radiation and the particle system. These interactions may be grouped together into

$$V^{R} = H^{eR} + H^{MR} \tag{1.15}$$

Substituting Eqs. (1.11) and (1.12) into Eq. (1.6) and employing

Eq. (1.15), the Hamiltonian becomes

$$H = H^e + H^{MX} + H^N + \mathcal{H}^I + V^R + H^R \tag{1.16}$$

1.2. PERTURBATION THEORY AND SCATTERING TRANSITIONS

There is no known method for proceeding directly from the Hamiltonian to a rigorous solution for a general radiation scattering problem. Thus we are led to introduce a form of perturbation theory. For this purpose the Hamiltonian as given by Eq. (1.16) is separated into a zero-order contribution H° and a perturbation V as follows:

$$H = H^\circ + V \tag{1.17}$$

We choose the separation defined by

$$H^\circ = H^e + H^{MX} + H^N + H^I + H^R \tag{1.18}$$

$$V = V^I + V^R \tag{1.19}$$

All the contributions to H and V have been defined previously except H^I and V^I. We require that

$$H^I + V^I = \mathcal{H}^I \tag{1.20}$$

H^I represents that part of the particle-particle interactions which is included in the zero-order Hamiltonian, whereas V^I represents the remaining part which is treated as a perturbation. It is desirable to choose H^I so that the zero-order internal states of molecules in the system will be factorable into individual states for each molecule. This requirement is satisfied if H^I is chosen to be any function of external coordinates only. Then it follows that the eigenfunctions of H°, defined by

$$H^0 \Psi_i^0 = E_i^0 \Psi_i^0 \tag{1.21}$$

may be chosen to factor into internal, external, and radiation state functions. In particular, the internal states satisfy

$$H^N |b\rangle = E_b^N |b\rangle \tag{1.22}$$

and since $H^N = \sum_{\alpha}^{N_M} H_\alpha^N$, these may be factored into individual particle internal state functions such that*

$$|b\rangle = |b_1\rangle |b_2\rangle \cdots |b_\alpha\rangle \cdots |b_{N_M}\rangle \tag{1.23}$$

where

$$H_\alpha^N |b_\alpha\rangle = E_{b_\alpha} |b_\alpha\rangle \tag{1.24}$$

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*Here we assume that the particles are separately distinguishable. This assumption is acceptable as long as the mean interparticle spacing is much greater than particle dimension and De Broglie wavelengths, a condition which prevails except under extreme pressure or very near absolute zero.

The external states are generated by the Hamiltonian

$$H^X = H^e + H^{XM} + H^I \tag{1.25}$$

such that

$$H^X|\mathcal{B}\rangle = E_{\mathcal{B}}|\mathcal{B}\rangle \tag{1.26}$$

In general these states do not factor into individual particle states as the internal states do because of H^I, which involves the external coordinates of all the particles in such a way that they cannot be separated into single particle additive contributions. However if H^I is neglected (ideal gas approximation) then the states $|\mathcal{B}\rangle$ can be chosen to factor as in Eq. (1.23).

The radiation states are generated by H^R as given by Eq. (1.2):

$$H^R|\eta\rangle = E_\eta|\eta\rangle \tag{1.27}$$

These states may be expressed as products of substates of well-defined polarization and propogation vectors[52]; i.e.,

$$|\eta\rangle = |\eta_1\rangle|\eta_2\rangle\cdots|\eta_\lambda\rangle\cdots \tag{1.28}$$

The quantum number η_λ represents the number of photons in the photon state of polarization $\underline{e}_\lambda$ and propogation vector $\underline{k}_\lambda$. The creation operators a_λ^+ and destruction operators a_λ introduced in Eqs. (1.2) and (1.3) operate on the radiation state as follows:

$$\alpha_\lambda^{\dagger}|\eta_1\rangle|\eta_2\rangle\cdots|\eta_\lambda\rangle\cdots = (\eta_\lambda+1)^{1/2}|\eta_1\rangle|\eta_2\rangle\cdots|\eta_\lambda+1\rangle\cdots \quad (1.29)$$

$$\alpha_\lambda|\eta_1\rangle|\eta_2\rangle\cdots|\eta_\lambda\rangle\cdots = \eta_\lambda^{1/2}|\eta_1\rangle|\eta_2\rangle\cdots|\eta_\lambda-1\rangle\cdots \quad (1.30)$$

The complete zero-order eigenfunctions are given by products of external, internal, and radiation state functions. They may be expressed in the form

$$\psi_i^0 = |\mathcal{B}\rangle|b\rangle|\eta\rangle \quad (1.31)$$

The state function for the system of particles and radiation, which satisfies the Schrodinger equation

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

may be expanded in terms of the zero-order wave functions as follows:

$$\Psi = \sum_j a_j(t)\psi_j^0$$

The quantity $|a_j(t)|^2$ is interpretable as the probability that the system will be in the state ψ_j^0 at time t. Suppose that the system is in state ψ_i^0 at t; then $a_j(t) = \delta_{ij}$. At a later time t+s, the probability that the system will be in an arbitrary state f is given by[54]

$$|a_f(t+s)|^2 = |U_{fi}(s)|^2 \quad (1.32)$$

where U(s) is the time-development operator of the system. If the Hamiltonian for the system is independent of time (as in the present case) then

$$U(s) = e^{-\frac{is}{\hbar}H} \quad (1.33)$$

In systems having continuous or dense state distributions in energy (as in the present case) perturbation theory approximations for the probability $|U_{fi}(s)|^2$ increase linearly with time in appropriate time domains. Anticipating this result, we define a transition probability <u>per unit time</u> from state i to state f by

$$T_{i\to f} = \frac{1}{s}\left| U_{fi}(s) \right|^2 \tag{1.34}$$

A goal of time-dependent perturbation theory is to calculate expressions for $T_{i\to f}$ to successive orders of approximation. In order to include the dominant features of light scattering from gases, it is necessary to carry the perturbation theory to second order at least, because in many cases the second order contribution will be comparable to or even larger than the first order contribution. (This point is discussed in Section 4.1.) On the other hand, the next higher order of approximation contains contributions associated with nonlinear radiation effects and other higher order corrections which we shall not examine in detail.* Thus we confine present attention to second order perturbation theory which leads to**

$$T_{i\to f} = \frac{2\pi}{\hbar}\left| V_{fi} - \sum_{g}{}' \frac{V_{fg}V_{gi}}{E_{gi}} \right|^2 \delta(E_{gi}) \tag{1.35}$$

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*See Sections 1.3, 1.5, 2.2, and 2.5 for remarks concerning these higher-order contributions.

**See, for example, Ref. 55, Sec. 4.3.

Near resonance or if initial and/or final states are significantly broadened or shifted in comparison with experimental resolution it is necessary to consider the effects of state widths and shifts on the scattering.* For this situation one may employ a form of perturbation theory known as damping theory. This approach is presented in basic form by Heitler[52]; Messiah[54] gives it a fairly detailed treatment and Akcasu[56] has developed and applied it with notable success to a variety of emission, absorption, and scattering problems in which line widths are important. Because for the most part we shall be interested in nonresonance scattering from particles whose initial and final states of concern are sharp, the discussion of the effects of energy widths and shifts on the scattering is relegated to Appendix B.

1.3. DEPENDENCE OF THE TRANSITION RATE PER UNIT TIME ON RADIATION STATES

In this section we determine an expression for the perturbation which is appropriate for a system of free electrons, ions, atoms, and molecules. Then the matrix elements and products of matrix elements of V which occur in $T_{i \to f}$ as given by Eq. (1.35) or (B-1) are evaluated between radiation states which are appropriate to a scattering transition.

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*The zero-order states, ψ_i^0, are characterized by sharply defined energies, eigenvalues of H^0. However, when these states are used to describe a system with Hamiltonian H^0+V, both a shift in energy and an energy uncertainty or width may become associated with each state.

From Eq. (1.19), the perturbation V may be written in the form

$$V = V^{I} + V^{R}$$

Notice that V^{I} contains no operators on the radiation states.

From Eqs. (1.15), (1.14) and (A.16), V^{R} can be written in the form

$$V^{R} = \sum_{j}^{N_e} \left[\frac{e}{mc} \underline{A}_j \cdot \underline{p}_j + \frac{e^2}{2mc^2} A_j^2 \right] + \sum_{\alpha}^{N_M} \sum_{j}^{Z_\alpha} \left[\frac{e}{mc} \underline{A}_{\alpha j} \cdot \underline{\Pi}_{\alpha j} + \frac{e^2}{2mc^2} A_{\alpha j}^2 \right] \tag{1.36}$$

Thus it appears that the light scattering is due primarily to the electrons of the system, bound and free, and that center-of-mass corrections may be ignored in the perturbation to a good approximation.

It is convenient to separate V^{R} into two parts as follows:

$$V^{R} = V^{1} + V^{2} \tag{1.37}$$

$$V^{1} = \sum_{j}^{N_e} \frac{e}{mc} \underline{A}_j \cdot \underline{p}_j + \sum_{\alpha}^{N_M} \sum_{j}^{Z_\alpha} \frac{e}{mc} \underline{A}_{\alpha j} \cdot \underline{\Pi}_{\alpha j} \tag{1.38}$$

$$V^{2} = \sum_{j}^{N_e} \frac{e^2}{2mc^2} A_j^2 + \sum_{\alpha}^{N_M} \sum_{j}^{Z_\alpha} \frac{e^2}{2mc^2} A_{\alpha j}^2 \tag{1.39}$$

This separation is useful because V^{1} is linear and V^{2} quadratic in creation and destruction operators. Thus, matrix elements of V^{1} vanish between all photon states except those which differ in only one occupation number, this number changing by one. Likewise, matrix elements of V^{2} vanish between all radiation states except those which are the same, or between which two occupation numbers are different, each changing by one, or between which only one occupation number is different, changing by two.

The dependence of the matrix elements involved in $T_{i\to f}$ on radiation states may now be determined. To do so, it is convenient to write out this quantity as given by Eq. (1.35), substituting from Eqs. (1.19) and (1.37) for V, and indicating explicitly the factorization of the zero order state functions into external particle, internal particle, and radiation functions. As a result one obtains

$$\begin{aligned} T_{\mathcal{B}b\eta\to\mathcal{B}'b'\eta'} = \frac{2\pi}{\hbar}\Big| & (V^1+V^2+V^I)_{\mathcal{B}'b'\eta',\,\mathcal{B}b\eta} \\ & -\sum_{\mathcal{B}''b''\eta''}\frac{1}{E_{\mathcal{B}''b''\eta''}-E_{\mathcal{B}b\eta}}\Big\{(V^1+V^2+V^I)_{\mathcal{B}'b'\eta',\,\mathcal{B}''b''\eta''} \\ & (\times)\,(V^1+V^2+V^I)_{\mathcal{B}''b''\eta'',\,\mathcal{B}b\eta}\Big\}\Big|^2\,\delta(E_{\mathcal{B}'b'\eta'}-E_{\mathcal{B}b\eta}) \end{aligned} \qquad (1.40)$$

At this point it is convenient to restrict attention to scattering transitions. If we write the initial radiation state in the form

$$|\eta\rangle = |\eta_1\rangle|\eta_2\rangle|\eta_R\rangle \qquad (1.41)$$

where $|\eta_1\rangle$ represents the photon state $\underline{\epsilon_1 k_1}$, $|\eta_2\rangle$ represents the photon state $\underline{\epsilon_2 k_2}$, and $|\eta_R\rangle$ represents the remaining photon states, then the final radiation state corresponding to a single scattering transition in which one photon is scattered from state $\underline{\epsilon_1 k_1}$ to state $\underline{\epsilon_2 k_2}$ is given by

$$|\eta'\rangle = |\eta_1-1\rangle|\eta_2+1\rangle|\eta_R\rangle \qquad (1.42)$$

Restricting attention to final states of this type we obtain from Eq. (1.40) the transition probability per unit time for a scattering interaction in which the particle states change from $\mathcal{B}b$ to $\mathcal{B}'b'$ and a photon is scattered from state $\underline{\epsilon}_1\underline{k}_1$ to state $\underline{\epsilon}_2\underline{k}_2$. Most of the matrix elements and matrix element products in Eq. (1.40) do not contribute to this transition probability because of the restriction on final photon states. In the first term within the absolute square, matrix elements of V^1 vanish since these are nonzero only between radiation states in which a single occupation number changes. Likewise, matrix elements of V^I vanish because this operator is diagonal between radiation states. In the second term within the absolute square, the products of matrix elements of V^1 with matrix elements of V^I and V^2 vanish because these are nonzero only between radiation states in which one or three photons change state.*

Products of matrix elements of V^2 contribute fourth-order corrections to the transition rate which correspond to nonlinear effects, and term which may be associated with corrections to the refractive index. As mentioned previously, these contributions will be neglected here.**

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*Actually the latter transition will contribute to observed scattering through events where two photons are absorbed and one is emitted, or vice versa. Consideration of these transitions and similar higher ordered transitions is excluded by our choice of final photon states. These transitions could be included by allowing a more general final photon state. However the resulting contribution to the scattering is of third order in the radiation particle coupling; it appears that this contribution is negligible at least under conditions of present interest (linear, nonresonance scattering and refraction index near unity).

**See Section 1.5 for a discussion of the significance of these terms.

Products of matrix elements of V^2 and V^I introduce corrections to the scattering rate which arise from particle-particle interactions. For scattering systems in which all particles are initially in nondegenerate ground states it can be argued that an appropriate choice for H^I, namely, $\langle b|\mathcal{H}^I|b\rangle$, will cause these contributions to be quite small. However, in systems in which internal particle states change frequently as a result of collisions it is possible that these terms might introduce significant corrections. These corrections will be ignored for the present but they are considered briefly in Sections 2.2 and 2.5.

Dropping the terms mentioned in the previous paragraphs, Eq. (1.40) becomes

$$T_{\mathcal{B}b\eta\to\mathcal{B}'b'\eta'} = \frac{2\pi}{\hbar}\Bigg| V^2_{\mathcal{B}'b'\eta',\mathcal{B}b\eta} - \sum_{\mathcal{B}''b''\eta''} \frac{1}{E_{\mathcal{B}''b''\eta''} - E_{\mathcal{B}b\eta}} V^1_{\mathcal{B}'b'\eta',\mathcal{B}''b''\eta''} V^1_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta} \Bigg|^2 \delta\left(E_{\mathcal{B}'\mathcal{B}} + E_{b'b} - \hbar\omega\right) \tag{1.43}$$

where

$$E_{\mathcal{B}'\mathcal{B}} \equiv E_{\mathcal{B}'} - E_{\mathcal{B}}$$

$$E_{b'b} \equiv E_{b'} - E_b$$

and

$$\hbar\omega = E_{\eta'} - E_{\eta} = \hbar c\left(k_1 - k_2\right)$$

Substituting from Eq. (1.3) for $\underline{A}(\underline{r})$ in Eqs. (1.38) and (1.39), one obtains expressions for V^1 and V^2 in terms of photon creation and destruction operators. The matrix elements of these operators between photon states may be evaluated immediately, using the properties outlined in Eqs. (1.29) and (1.30). One obtains for the matrix elements of V^2

between the photon states given by Eqs. (1.41) and (1.42):

$$V^2_{\mathcal{B}'b'\eta',\mathcal{B}b\eta} = \left(\frac{e^2}{mc^2}\right)\left(\frac{2\pi\hbar c}{L^3}\right)\left[\frac{\eta_1(1+\eta_2)}{k_1 k_2}\right]^{1/2}(\underline{\epsilon}_1\cdot\epsilon_2) \tag{1.44}$$

$$(\times)\left[\langle\mathcal{B}'|\sum_j^{N_c} e^{i\underline{K}\cdot\underline{r}_j}|\mathcal{B}\rangle + \sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|e^{i\underline{K}\cdot\underline{\rho}_{\alpha j}}|b\rangle\right]$$

where

$$\underline{K} \equiv \underline{k}_1 - \underline{k}_2$$

This contribution will be referred to as the first-order contribution to the scattering. The reference is not to relative magnitude, but to the sequence in the perturbation expansion.

The products of matrix elements in the second part of Eq. (1.43) involve intermediate radiation states represented by $|\eta''\rangle$. Because of the properties of V^1, there are only two types of intermediate radiation states for which the products of matrix elements do not vanish. These are:

(a) $|\eta''\rangle = |\eta_1 - 1\rangle|\eta_2\rangle|\eta_R\rangle$

(b) $|\eta''\rangle = |\eta_1\rangle|\eta_2 + 1\rangle|\eta_R\rangle$

Evaluating these matrix elements between photon states, one obtains

Case (a): (1.45)

$$\frac{V^1_{\mathcal{B}'b'\eta',\mathcal{B}''b''\eta''}V^1_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}}{E_{\mathcal{B}''b''\eta''} - E_{\mathcal{B}b\eta}} = \left(\frac{e}{mc}\right)^2\left(\frac{2\pi\hbar c}{L^3}\right)\left[\frac{\eta_1(1+\eta_2)}{k_1 k_2}\right]\frac{1}{E_{\mathcal{B}''\mathcal{B}} + E_{b''b} - \hbar\omega_1}$$

$$(\times)\left[\sum_l^{N_e}\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{r}_l}p_{l2}|\mathcal{B}\rangle\delta_{b'b''} + \sum_\beta^{N_M}\sum_l^{Z_\beta}\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\beta}|\mathcal{B}''\rangle\langle b'|e^{-i\underline{k}_2\cdot\underline{\rho}_{\beta l}}\pi_{\beta l 2}|b''\rangle\right]$$

$$(\times)\left[\sum_j^{N_e}\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}\rangle\delta_{b''b} + \sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b''|e^{i\underline{k}_1\cdot\underline{\rho}_{\alpha j}}\pi_{\alpha j 1}|b\rangle\right]$$

Case (b):

(1.46)

$$\frac{V'_{\mathcal{B}'b'\eta',\mathcal{B}''b''\eta''}\,V'_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}}{E_{\mathcal{B}''b''\eta''}-E_{\mathcal{B}b\eta}} = \left(\frac{e}{mc}\right)^2\left(\frac{2\pi\hbar c}{L^3}\right)\left[\frac{\eta_1(1+\eta_2)}{k_1 k_2}\right]\frac{1}{E_{\mathcal{B}''\mathcal{B}}+E_{b''b}-\hbar\omega_2}$$

$$(\times)\left[\sum_j^{N_e}\langle\mathcal{B}'|e^{i\mathbf{k}_1\cdot\mathbf{r}_j}p_{j1}|\mathcal{B}''\rangle\delta_{b'b''}+\sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}'|e^{i\mathbf{k}_1\cdot\mathbf{R}_\alpha}|\mathcal{B}''\rangle\langle b'|e^{i\mathbf{k}_1\cdot\boldsymbol{\rho}_{\alpha j}}\pi_{\alpha j1}|b''\rangle\right]$$

$$(\times)\left[\sum_l^{N_e}\langle\mathcal{B}''|e^{-i\mathbf{k}_2\cdot\mathbf{r}_l}p_{l2}|\mathcal{B}\rangle\delta_{b''b}+\sum_\beta^{N_M}\sum_l^{Z_\beta}\langle\mathcal{B}''|e^{-i\mathbf{k}_2\cdot\mathbf{R}_\beta}|\mathcal{B}\rangle\langle b''|e^{-i\mathbf{k}_2\cdot\boldsymbol{\rho}_{\beta l}}\pi_{\beta l2}|b\rangle\right]$$

Here we have introduced the notation $\pi_{\alpha j\lambda} = \boldsymbol{\epsilon}_\lambda\cdot\pi_{\alpha j}$, etc. These contributions will be referred to as the second order contributions to the scattering.

Substituting Eqs. (1.44), (1.45) and (1.46) into Eq. (1.43), one obtains

(1.47)

$$T_{\mathcal{B}b\eta\rightarrow\mathcal{B}'b'\eta'} = \frac{2\pi}{\hbar}\left(\frac{e^2}{mc^2}\right)^2\left(\frac{2\pi\hbar c}{L^3}\right)^2\frac{\eta_1(1+\eta_2)}{k_1k_2}\,\delta(E_{\mathcal{B}'\mathcal{B}}+E_{b'b}-\hbar\omega)$$

$$(\times)\Bigg|(\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2)\sum_j^{N_e}\langle\mathcal{B}'|e^{i\mathbf{K}\cdot\mathbf{r}_j}|\mathcal{B}\rangle\delta_{b'b}+(\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2)\sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}'|e^{i\mathbf{K}\cdot\mathbf{R}_\alpha}|\mathcal{B}\rangle\langle b'|e^{i\mathbf{K}\cdot\boldsymbol{\rho}_{\alpha j}}|b\rangle$$

$$-\frac{1}{m}\sum_{\mathcal{B}''b''}\Bigg\{\frac{1}{E_{\mathcal{B}''\mathcal{B}}+E_{b''b}-\hbar\omega_1}\left[\sum_l^{N_e}\langle\mathcal{B}'|e^{-i\mathbf{k}_2\cdot\mathbf{r}_l}p_{l2}|\mathcal{B}''\rangle\delta_{b'b''}+\sum_\beta^{N_M}\sum_l\langle\mathcal{B}'|e^{-i\mathbf{k}_2\cdot\mathbf{R}_\beta}|\mathcal{B}''\rangle\langle b'|e^{-i\mathbf{k}_2\cdot\boldsymbol{\rho}_{\beta l}}\pi_{\beta l2}|b''\rangle\right]$$

$$(\times)\left[\sum_j^{N_e}\langle\mathcal{B}''|e^{i\mathbf{k}_1\cdot\mathbf{r}_j}p_{j1}|\mathcal{B}\rangle\delta_{b''b}+\sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}''|e^{i\mathbf{k}_1\cdot\mathbf{R}_\alpha}|\mathcal{B}\rangle\langle b''|e^{i\mathbf{k}_1\cdot\boldsymbol{\rho}_{\alpha j}}\pi_{\alpha j1}|b\rangle\right]$$

$$+\frac{1}{E_{\mathcal{B}''\mathcal{B}}+E_{b''b}+\hbar\omega_2}\left[\sum_j^{N_e}\langle\mathcal{B}'|e^{i\mathbf{k}_1\cdot\mathbf{r}_j}p_{j1}|\mathcal{B}''\rangle\delta_{b'b''}+\sum_\alpha^{N_M}\sum_j^{Z_\alpha}\langle\mathcal{B}'|e^{i\mathbf{k}_1\cdot\mathbf{R}_\alpha}|\mathcal{B}''\rangle\langle b'|e^{i\mathbf{k}_1\cdot\boldsymbol{\rho}_{\alpha j}}\pi_{\alpha j1}|b''\rangle\right]$$

$$(\times)\left[\sum_l^{N_e}\langle\mathcal{B}''|e^{-i\mathbf{k}_2\cdot\mathbf{r}_l}p_{l2}|\mathcal{B}\rangle\delta_{b''b}+\sum_\beta^{N_M}\sum_l^{Z_\beta}\langle\mathcal{B}''|e^{-i\mathbf{k}_2\cdot\mathbf{R}_\beta}|\mathcal{B}\rangle\langle b''|e^{-i\mathbf{k}_2\cdot\boldsymbol{\rho}_{\beta l}}\pi_{\beta l2}|b\rangle\right]\Bigg\}\Bigg|^2$$

It is convenient at this point to introduce the dipole approximation, expanding the exponentials $e^{i\underline{k}\cdot\underline{\rho}_{\alpha j}}$, etc., involved in matrix elements between internal states, and neglecting all but the leading terms (unity). This approximation appears to be very good for light scattering from atoms, ions, and simple molecules because the wavelengths involved are several orders of magnitude greater than the particle dimensions and therefore $\underline{k}\cdot\underline{\rho}_{\alpha j} \ll 1$ over values of $\underline{\rho}_{\alpha j}$ for which the internal wave functions are significantly different from zero. Thus the quadrupole and higher order scattering transition which we neglect in the dipole approximation are, in general, very weak.

Adopting this approximation and at the same time multiplying out the terms within the absolute square in Eq. (1.47), one obtains Eq. (C.1). This equation is not reproduced here because of its complexity. Much of this complexity arises from the cross products within the absolute square of matrix elements involving different particles. These cross terms give rise to scattering transitions in which two particles may change states simultaneously. For example, both particles might absorb energy from an incident photon during a single scattering transition. In Appendix C it is demonstrated that these contributions vanish in the ideal gas approximation. Moreover, it appears that the cross terms between molecule pairs, and between molecule and electron pairs should be very small in a real gas, or plasma at least away from resonance. However, it is not immediately clear that cross terms between pairs of free electrons are small in, say, a plasma. Accordingly we will retain the electron cross terms for the moment but drop all others to obtain a much simplified expression for $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$ which should be accurate at least away from resonance. This expression is

$$
\begin{aligned}
T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'} &= \frac{2\pi}{\hbar^2}\left(\frac{e^2}{mc^2}\right)^2\left(\frac{2\pi\hbar c}{L^3}\right)^2\left[\frac{\eta_1(1+\eta_2)}{k_1 k_2}\right]\delta(\omega_{\mathcal{B}'\mathcal{B}}+\omega_{b'b}-\omega) \\
(x)\ \Bigg| & (\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\sum_{j}^{N_e}\langle\mathcal{B}'|e^{i\underline{k}\cdot\underline{r}_j}|\mathcal{B}\rangle\delta_{b'b} + (\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\sum_{\alpha}^{N_M} Z_\alpha\langle\mathcal{B}'|e^{i\underline{k}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\delta_{b'b} \\
&+ \frac{\delta_{b'b}}{\hbar m}\sum_{\mathcal{B}''}\sum_{jl}^{N_e}\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{r}_l}p_{l2}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}} - \frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{r}_l}p_{l2}|\mathcal{B}\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}}\right\} \\
&+ \frac{1}{\hbar m}\sum_{\mathcal{B}''b''}\sum_{\alpha}^{N_M}\left\{\frac{1}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}-\omega_{b''b}}\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle\right. \\
&\left. - \frac{1}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}+\omega_{b''b}}\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle\right\}\Bigg|^2
\end{aligned}
\tag{1.48}
$$

Here we have introduced the notation

$$\Pi_{\alpha 1} \equiv \sum_{j}^{Z_\alpha}\Pi_{\alpha j 1}$$

$$\omega_{\mathcal{B}''\mathcal{B}} = \frac{1}{\hbar}(E_{\mathcal{B}''}-E_{\mathcal{B}})$$

In the following section the relationship between $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$ and scattering cross sections will be developed.

1.4. RELATIONSHIPS BETWEEN $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$, SCATTERING CROSS SECTIONS AND INTENSITY OF SCATTERED RADIATION

Scattering cross sections appear to be more convenient than transition probabilities for describing the scattering properties of a general system. Accordingly, we define the differential scattering cross section

$\sigma(\underline{\epsilon}_1\underline{k}_1 \to \underline{\epsilon}_2\underline{k}_2)$ such that

$$\sigma(\underline{\epsilon}_1\underline{k}_1 \to \underline{\epsilon}_2\underline{k}_2)d^3k_2 = \frac{\begin{array}{l}\text{Rate at which photons are scattered from an}\\ \text{initial state of polarization } \underline{\epsilon}_1 \text{ and propogation vector } \underline{k}_1 \text{ to a final state with polarization } \underline{\epsilon}_2 \text{ and propogation vector in } d^3k_2 \text{ at } \underline{k}_2\end{array}}{N\ (x) \text{ incident photon flux}} \tag{1.49}$$

In Chapter II it will become apparent that this cross section is independent of the cell dimension L, as implied in Section 2.1. We proceed now to develop the relationship between this quantity and $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$ as given by Eq. (1.48).

The transition probability per unit time $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$ corresponds to a transition between a specific initial state and specific final state. However, during the course of a typical scattering experiment, the initial and final <u>particle</u> states are not observed. In fact, the most that one usually knows about the particle system is some of its statistical properties such as temperature and average density. We assume here that the statistical nature of the scattering system is properly handled by an appropriate average of $T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'}$ over all unobserved initial particle states and sum over all unobserved final particle states. On the other hand we assume that the initial radiation state is fixed by observation.

Representing by $P_{\mathcal{B}b}$ the probability that the external particle state is $|\mathcal{B}>$ and the internal particle state is $|b>$, we obtain

$$T_{\eta \to \eta'} = \sum_{\mathcal{B}b} \sum_{\mathcal{B}'b'} P_{\mathcal{B}b}\, T_{\mathcal{B}b\eta \to \mathcal{B}'b'\eta'} \tag{1.50}$$

This quantity represents the probability per unit time that a photon will be scattered from state $\underline{\epsilon}_1\, \underline{k}_1$ to state $\underline{\epsilon}_2\, \underline{k}_2$ in a system whose statistical properties are represented by $P_{\mathrm{B}b}$. However one would like to know the probability per unit time that photons will be scattered into final states of polarization $\underline{\epsilon}_2$ whose propogation vectors lie in the small increment $\Delta^3 k_2$ about $\underline{k}_2$. This quantity is obtained by summing $T_{\eta\to\eta'}$ over all final states of the specified polarization which lie in $\Delta^3 k_2$. From Eq. (1.4), the number of such states is given by $(L/2\pi)^3 \Delta^3 k_2$, where L is the cell dimension. If $\Delta^3 k_2$ is sufficiently small, then $T_{\eta\to\eta'}$ will not vary significantly over the sum and one obtains

$$\sum_{\eta' \, in \, \Delta^3 k_2} T_{\eta\to\eta'} = \left(\frac{L}{2\pi}\right)^3 \Delta^3 k_2\, T_{\eta\to\eta'} \tag{1.51}$$

The cross section defined by Eq. (1.49) may now be obtained from Eq. (1.51) upon dividing by the incident photon flux within the cell, $(\eta_1 c/L^3)$, and the number of scattering particles. Thus

$$\sigma(\underline{\epsilon}_1 \underline{k}_1 \to \underline{\epsilon}_2 \underline{k}_2) = \frac{1}{N}\left(\frac{L^3}{\eta_1 c}\right)\left(\frac{L}{2\pi}\right)^3 T_{\eta\to\eta'} \tag{1.52}$$

We wish to develop the relation between this cross section, which pertain to scattering in a cell, and the intensity of scattered radiation which will be observed in an experiment. Before doing so it is necessary to note that the radiation within the cell has been expanded in a momentum representation. In this representation the radiation is treated as if it were distributed uniformly over the cell. Thus our analysis of scattering within a large cell corresponds to an experiment in which the intensity of incident radiation is uniform over a sufficiently large scattering volume.* This incident radiation may be described by $I(\underline{\epsilon}\,\underline{k})$ which is defined such that

$$I(\underline{\epsilon}\,\underline{k})d^3k \;=\; \begin{array}{l}\text{intensity of incident radiation with polarization } \underline{\epsilon} \\ \text{and propogation vector in } d^3k \text{ at } \underline{k}.\end{array} \tag{1.53}$$

Here the intensity is measured in terms of energy crossing unit area (normal to $\underline{k}$) per unit time. The incident photon flux in the state $\underline{\epsilon}_\lambda\,\underline{k}_\lambda$ is given in terms of $I(\underline{\epsilon}\,\underline{k})$ by

$$\left(\frac{n_\lambda c}{L^3}\right) = \frac{1}{\hbar c k_\lambda}\left(\frac{2\pi}{L}\right)^3 I(\underline{\epsilon}_\lambda \underline{k}_\lambda) \tag{1.54}$$

The number of scattered photons with polarization $\underline{\epsilon}_2$ and propogation vectors in d^3k_2 about $\underline{k}_2$ which appear per unit time and volume is obtained by multiplying the cross section defined in Eq. (1.49) by the incident photon flux in state $\underline{\epsilon}_\lambda\,\underline{k}_\lambda$, then summing over all initial photon states. The cell is required to be large enough so that neither the incident intensity nor the cross section change significantly between adjacent radiation states. Then to a good approximation the sum over $\underline{k}_\lambda$ may be replaced by an integral through the relation

$$\sum_{k_\lambda} \to \left(\frac{L}{2\pi}\right)^3 \int d^3k$$

---

*The scattering volume is defined to be the volume common to the incident beam and scattering particles which is observed by the detector of scattered radiation. The lower limit on the dimension of the scattering volume, beyond which the present results are not clearly valid, is discussed in Section 1.5.

and one obtains for the total number of photons scattered into states with polarization $\underline{\epsilon}_2$ and propogation vectors in d^3k_2 about $\underline{k}_2$ per unit time and unit volume*

$$d^3k_2 \sum_{\lambda} \int d^3k_1 \frac{1}{\hbar c k_1} I(\underline{\epsilon}_\lambda \underline{k}_1) N_0 \sigma(\underline{\epsilon}_\lambda \underline{k} \rightarrow \underline{\epsilon}_2 k_2) \qquad (1.55)$$

Here N_0 is the average density of scattering particles: i.e.,

$$N_0 = \frac{N}{L^3}$$

The intensity of scattered radiation at a point R measured from the scattering volume is obtained by multiplying (1.55) by the scattering volume V_s and the energy per scattered photon $\hbar\omega_2$, and dividing by R^2. (We make the usual assumption that R is much greater than the largest dimension of the scattering volume.) Defining $I_s(R|\underline{\epsilon_2 k_2})$ such that

$I_s(R|\underline{\epsilon_2 k_2})d^3k_2$ = intensity of scattered radiation at $\underline{R}$ with polarization $\underline{\epsilon}_2$ and propogation vector in d^3k_2 at $\underline{k}_2$

we obtain

$$I_s(R|\underline{\epsilon}_2 \underline{k}_2) = \frac{V_s N_0}{R^2} \sum_{\lambda} \int d^3k_1 \frac{k_2}{k_1} I(\underline{\epsilon}_\lambda \underline{k}_1) \sigma(\underline{\epsilon}_\lambda \underline{k}_1 \rightarrow \underline{\epsilon}_2 \underline{k}_2) \qquad (1.56)$$

It is convenient to express the cross section and intensities in terms of frequencies and directions of propogation rather than in terms of propogation vectors. This transformation is easily effected, and one

---

*The sum over λ now indicates a sum over the two possible polarization associated with a particle propogation vector $\underline{k}$. The dependence of the polarization vector on $\underline{k}$ can be indicated by writing these unit vector in the form $\underline{\epsilon}_\lambda(\underline{k})$; however, we have shortened the notation to $\underline{\epsilon}_\lambda$.

obtains (using the free space dispersion relation $\hbar c k_\lambda = \hbar\omega_\lambda$)

$$I_S(R|\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{V_S N_0}{R^2}\sum_\lambda \int d\omega_1 d\Omega_1 \frac{\omega_2}{\omega_1} I(\underline{\epsilon}_\lambda\omega_1\underline{\Omega}_1)\sigma(\underline{\epsilon}_\lambda\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) \tag{1.57}$$

and

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = c^{-1} k_2^2\, \sigma(\underline{\epsilon}_1\underline{k}_1 \to \underline{\epsilon}_2\underline{k}_2) \tag{1.58}$$

From Eqs. (1.58), (1.52), (1.50) and (1.48)

$$\begin{aligned}
\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) &= \frac{1}{N}\frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}\mathcal{B}'}\sum_{bb'} P_{\mathcal{B}b}\,\delta(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega) \\
(\times)\Bigg|(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)&\sum_j^{N_e}\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{r}_j}|\mathcal{B}\rangle\delta_{b'b} + \underline{\epsilon}_1\cdot\underline{\epsilon}_2\sum_\alpha^{N_M} Z_\alpha\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\delta_{b'b} \\
+\frac{\delta_{b'b}}{\hbar m}\sum_{j\ell}^{N_e}\sum_{\mathcal{B}''}&\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{r}_\ell}p_{\ell 2}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}\rangle}{\omega_1 - \omega_{\mathcal{B}''\mathcal{B}}} - \frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{r}_\ell}p_{\ell 2}|\mathcal{B}\rangle}{\omega_2 + \omega_{\mathcal{B}''\mathcal{B}}}\right\} \\
+\frac{1}{\hbar m}\sum_\alpha^{N_M}\sum_{\mathcal{B}''b''}&\left\{\frac{1}{\omega_1 - \omega_{\mathcal{B}''\mathcal{B}} - \omega_{b''b}}\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle\right. \\
&\left.- \frac{1}{\omega_2 + \omega_{\mathcal{B}''\mathcal{B}} + \omega_{b''b}}\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle\right\}\Bigg|^2
\end{aligned} \tag{1.59}$$

The occupation number η_2 in Eq. (1.48) contributes to stimulated scattering. Since we are not specifically concerned with stimulated scattering here, this contribution has been neglected in Eq. (1.59). This equation for the scattering cross section will serve as the starting point for most of the work in Chapters II, III, and IV.*

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*Note that the sums over internal and external states in Eq. (1.59) imply integrals over continuously distributed eigenvalues. In particular, the sum over b" implies an integral over the continuously distributed eigenvalues of the positive energy states of molecules as well as sums over the discrete eigenvalues of both positive and negative energy states.

1.5. DISCUSSION OF THE CROSS SECTION DERIVATION

As noted in Section 1.4, the results of that section apply to a system in which the properties of the incident radiation are constant over a "large" scattering volume. Here we wish to establish what is meant by "large." The effects of spatial variations of radiation properties may be examined by breaking up the scattering volume into small cells over which these properties do not change significantly, then calculating the scattering contributions from each cell. Osborn[57] and Klevans[58] have developed the small cell approach in connection with problems of radiation transport. Taking their work into account, it appears that as long as the dimensions of the cells are much larger than wavelengths or correlation ranges of interest,* spatial variations in these properties (within the limits of linear response) should not affect the cross section.

On the other hand, as the diameter of the incident beam becomes very small, the properties of the scattered radiation may depend significantly on the shape of the scattering volume. For example, this situation may arise in light scattering from solids and liquids. Here the scattering per molecule is reduced, typically, by an order of magnitude

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*By correlation range of interest is meant a range over which significant correlations between motions of different particles exists in the scattering system, <u>and</u> observably affect the scattering. Very long range correlations exist in a large crystal, but the entire range may not be of interest in the present respect because the longer range correlations affect only the unresolved fine detail of the scattering. See Ref. 50 for a brief but lucid discussion of correlation ranges in various media.

by interference from different parts of the scattering volume. If the scattering volume is made extremely small such that its dimensions approach the incident and scattering wavelengths, the interference may be less complete and the scattering correspondingly stronger. Somewhat similar effects may arise for scattering from plasmas or systems near a critical point.

Theimer[59] has suggested that the shape of the scattering volume may affect the scattering even in ideal gases. It may be possible to investigate this situation from a quantum approach through methods such as those developed by Osborn and Klevans. However, such an undertaking appears to be a difficult, separate problem, and will not be considered further here.

Several times in Chapter I we have used the free space dispersion relation

$$\hbar c k_\lambda = E_\lambda = \hbar \omega_\lambda$$

where E_λ is the photon energy in state λ. This relation is consistent with the radiation Hamiltonian given by Eq. (1.2). In the ensuing straightforward development of the radiation—particle interaction, higher-order corrections which may be associated with a nonunity refractive index appear in terms of the perturbation expansion which have been omitted. This approximation appears to be acceptable in gaseous or plasma systems at least well away from resonance. However, such corrections can be included to a certain approximation through a method developed by Mead.[60] This method involves the introduction of a slightly modified radiation Hamiltonian containing an arbitrary parameter which can be adjusted to cause the most significant of the higher order contributions to the refractive index to vanish. As a result, these contributions are incorporated through the parameter into the lower order terms. This so-called photon dressing can be introduced into the development of this chapter without great difficulty.

In obtaining Eq. (1.59), the effects of nonlinear scattering have been neglected consistently. Since these effects are accessible at least using presently available giant pulse lasers,* some care ought to be taken to examine the possible significance of nonlinear scattering in any experiment employing high intensity incident light. Theoretical considerations of this problem have already been mentioned.[43] However, George and coworkers[61] have observed no evidence of nonlinear scattering at moderate laser beam intensities, nor have Watson and Clark.[62]

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*One clear example occurs when the laser beam breaks down a gaseous scattering system, turning it into a plasma. This well known phenomenon can be demonstrated by carefully focussing the beam of any quality 10 Mw laser. Observations of less drastic nonlinear scattering in gases are not known to the author, although this phenomenon is being observed in liquids and solids.

CHAPTER II

THE DEPENDENCE OF LIGHT SCATTERING CROSS SECTIONS ON EXTERNAL STATES

It is evident from the energy-conserving δ-function in the general cross section as given by Eq. (1.59) that the frequency distribution of light scattered from a monochromatic beam in a gas or plasma is determined by energy exchanges between the incident photons and the internal and external states of the scattering system. From experiment it appears that the various possible energy exchanges with discrete internal states determine the location of spectral lines of scattered light. These energy exchanges may range from zero to amounts comparable to the energy of the incident photon. In contrast, energy exchanges with the external states in a gas or plasma are continuously distributed and are usually extremely small, being on the order of 10^{-6} times the incident photon energy for light scattering from atoms. These small energy exchanges depend on particle motions and particle-particle interactions; they play a major role in determining the detailed shapes of the spectral lines of scattered light.

In this chapter the dependence of light scattering cross sections on external states is expressed in terms of two-time correlation functions of particle positions, namely, the Van Hove G-functions.[49] Although this formulation is not necessarily the best for the purpose of calculating light scattering cross sections, the clear and simple physical interpretation of the classical limits of the G-functions and the connection established with the many other subjects in which the G-functions have been involved makes it interesting and worthwhile. Moreover, fairly good calculations of the G-functions (or rather, their classical limits) for many systems of interest are available or being developed rapidly, so that where a formulation of scattering cross sections in terms of G-functions is valid, the dependence on external states may often be estimated quickly.

Previously, from the classical fluctuation theory of light scattering, Pecora[16] has argued that the scattering cross sections might be expressed in terms of classical limits of the G-functions. On the other hand, Sjörlander[50] has noted that while "direct" light scattering* can be expressed in terms of G-functions, if scattering transitions through intermediate states are significant then the quantum light scattering cross section is not related rigorously to the G-functions, but rather to more complicated correlations involving an additional time variable.

It is argued in Section 4.1 that transitions through intermediate states play an important role in light scattering from atoms and molecules. However, we are able to show in Section 2.1 that the corresponding light scattering cross sections may be expressed in terms of the Van Hove G-functions through an approximation which appears to be satisfied very well in many nonresonance light scattering experiments. In

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*That is, scattering which arises predominantly from the first-order contribution of the perturbation theory.

Sections 2.2 and 2.3, properties of the G-functions and their classical limits are employed to discuss the detailed shape of spectral lines of scattered radiation. In Section 2.4 the cross section integrated over a particular spectral line of the scattered radiation is related to a single time correlation function through the so-called static approximation, and the properties of this cross section which depend on external states are discussed. Finally, in Section 2.5, some limitations to the G-function formulation are pointed out.

2.1. THE CROSS SECTION IN TERMS OF CORRELATION FUNCTIONS

The light scattering cross section as given by Eq. (1.59) is the starting point for the work in this section. Drawing upon the arguments of Chapter III, it is assumed that the resonance contributions to the free electron scattering may be ignored. As a result, Eq. (1.59) becomes

$$\begin{aligned}\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\epsilon_2\omega_2\Omega_2) &= \frac{1}{N}\frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\mathcal{B}'\mathcal{B}}\sum_{b'b}P_{\mathcal{B}b}\,\delta(\omega_{\mathcal{B}'\mathcal{B}}+\omega_{b'b}-\omega)\\ &(\times)\Bigg|(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\sum_{j}^{N_e}\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{r}_j}|\mathcal{B}\rangle+(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\sum_{\alpha}^{N_M}Z_\alpha\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\delta_{b'b}\\ &+\frac{1}{\hbar m}\sum_{\alpha}^{N_M}\sum_{\mathcal{B}''b''}\Bigg\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}-\omega_{b''b}}\\ &-\frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}+\omega_{b''b}}\Bigg\}\Bigg|^2\end{aligned} \tag{2.1}$$

In this equation the dependence of the first-order terms on external coordinates is not the same as that of the second-order terms, complicating any attempt to separate the external state contributions to the cross section from the internal state contributions. This complication can be removed if it is possible to ignore $\omega_{\mathcal{B}''\mathcal{B}}$ in the denominators of the resonance terms and sum over $\mathcal{B}''$, employing the closure property of the external state functions. In Appendix D it is shown that in the ideal gas the error introduced by ignoring $\omega_{\mathcal{B}''\mathcal{B}}$ is of order $v/c\left(\omega_1/\omega_1-\omega_{b''b}\right)$ in the first term and $v/c\left(\omega_1/\omega_2+\omega_{b''b}\right)$ in the second term. Here v is the velocity of a typical scattering particle. Therefore the error introduced in the ideal gas approximation by ignoring $\omega_{\mathcal{B}''\mathcal{B}}$ will be negligible when the separation from resonance is large compared to the Doppler broadening of corresponding emission lines—a small fraction of an angstrom at room temperature.

In a real gas, experimental observations of the sharpness of emission spectral lines support the conclusion that $\omega_{\mathcal{B}''\mathcal{B}}$ will still be small for those matrix elements $\langle \mathcal{B}''|e^{i\underline{k}\cdot\underline{R}}|\mathcal{B}\rangle$ which are significant. If the separation from resonance is much greater than $\omega_{\mathcal{B}''\mathcal{B}}$ for these matrix elements then it appears that to a good approximation one may ignore $\omega_{\mathcal{B}''\mathcal{B}}$ and sum over $\mathcal{B}''$ in Eq. (2.1) to obtain

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{1}{N}\frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}'\mathcal{B}}\sum_{b'b} P_{\mathcal{B}b}\,\delta(\omega_{\mathcal{B}'\mathcal{B}}+\omega_{b'b}-\omega) \tag{2.2}$$

$$(\times)\left|\sum_{\alpha}^{N}\langle \mathcal{B}'|e^{i\underline{k}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle a_{\alpha b'b}\right|^2$$

Here we have defined

$$a_{\alpha b'b} = (\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\delta_{b'b}\ , \quad 1 \leq \alpha \leq N_e \tag{2.3}$$

and for $N_e < \alpha \leq N_e + N_M$,

$$a_{\alpha b'b} = (\underline{\epsilon}_1 \cdot \underline{\epsilon}_2) Z_\alpha \delta_{b'b} + \frac{1}{\hbar m} \sum_{b''} \left\{ \frac{\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle}{\omega_1 - \omega_{b''b}} - \frac{\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle}{\omega_2 + \omega_{b''b}} \right\} \tag{2.4}$$

Near room temperature in a neutral gas, separation from resonance by 10^{12} sec^{-1}, or in terms of wavelength, by one angstrom or more, is probably a sufficient criterion for the validity of Eq. (2.2).

In order to develop the relationship between Eq. (2.2) and particle correlation functions, it is convenient to introduce

$$\delta(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{i(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega)}$$

Substituting this expression for the Dirac δ-function in Eq. (2.2), the cross section becomes

$$\sigma(\underline{\epsilon}_1 \omega_1 \underline{\Omega}_1 \rightarrow \underline{\epsilon}_2 \omega_2 \underline{\Omega}_2) = \frac{\omega_2}{2\pi N \omega_1} \left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}'\mathcal{B}} \sum_{b'b} P_{\mathcal{B}b} \tag{2.5}$$

$$(\mathsf{X}) \int_{-\infty}^{\infty} d\tau\, e^{i(\omega_{b'b} - \omega)\tau} \sum_{\alpha\alpha'} a^*_{\alpha b'b} a_{\alpha' b'b} \langle \mathcal{B}| e^{-i\underline{K}\cdot\underline{R}_\alpha} e^{\frac{i\tau}{\hbar}H^\times} |\mathcal{B}'\rangle\langle\mathcal{B}'| e^{i\underline{K}\cdot\underline{R}_{\alpha'}} e^{-\frac{i\tau}{\hbar}H^\times} |\mathcal{B}\rangle$$

Now the sum over $\mathcal{B}'$ may be carried out directly, invoking the closure property of the external state functions, to obtain

$$\sigma(\underline{\epsilon}_1 \omega_1 \underline{\Omega}_1 \rightarrow \underline{\epsilon}_2 \omega_2 \underline{\Omega}_2) = \frac{\omega_2}{2\pi N \omega_1} \left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}} \sum_{b'b} P_{\mathcal{B}b} \tag{2.6}$$

$$(\mathsf{X}) \int_{-\infty}^{\infty} d\tau\, e^{i(\omega_{b'b} - \omega)\tau} \sum_{\alpha\alpha'} a^*_{\alpha b'b} a_{\alpha' b'b} \langle \mathcal{B}| e^{-i\underline{K}\cdot\underline{R}_\alpha} e^{\frac{i\tau}{\hbar}H^\times} e^{i\underline{K}\cdot\underline{R}_{\alpha'}} e^{-\frac{i\tau}{\hbar}H^\times} |\mathcal{B}\rangle$$

It is convenient to introduce the expansion

$$e^{\frac{i\tau}{\hbar}H^x} e^{i\underline{k}\cdot\underline{R}_{\alpha'}} e^{-\frac{i\tau}{\hbar}H^x} = \sum_n \frac{1}{n!}\left(\frac{i\tau}{\hbar}\right)^n \left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^n \tag{2.7}$$

where by definition

$$\left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^0 = e^{i\underline{k}\cdot\underline{R}_{\alpha'}}$$

$$\left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^1 = \left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]$$

$$\left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^2 = \left[H^x, \left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]\right]$$

and so forth. The operator

$$\left(\frac{i}{\hbar}\right)^n \left[H^x, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^n$$

represents the n^{th} time derivative of $e^{i\underline{k}\cdot\underline{R}_{\alpha}'}$ in a system described by the Hamiltonian H^x, that is, a system of particles whose mutual interactions are functions only of the distances between their centers. In this type of system the series in Eq. (2.7) is in the form of a Taylor expansion in time, and may be represented by the operator $e^{i\underline{k}\cdot\underline{R}_{\alpha}'(\tau)}$ in the Heisenberg scheme. In the same scheme $e^{-i\underline{k}\cdot\underline{R}_{\alpha}}$ may be written $e^{-i\underline{k}\cdot\underline{R}_{\alpha}(0)}$. Introducing this notation into Eq. (2.6), the expression for the scattering cross section becomes

$$\sigma(\underline{\epsilon}_1\omega_1\Omega_1 \rightarrow \underline{\epsilon}_2\omega_2\Omega_2) = \frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}} \sum_{b'b} P_{\mathcal{B}b}$$

$$(x) \sum_{\alpha\alpha'} a^*_{\alpha b'b} a_{\alpha' b'b} \int d\tau\, e^{i(\omega_{b'b}-\omega)\tau} \langle \mathcal{B}| e^{-i\underline{k}\cdot\underline{R}_{\alpha}(0)} e^{i\underline{k}\cdot\underline{R}_{\alpha'}(\tau)} |\mathcal{B}\rangle \tag{2.8}$$

It is convenient to break up this cross section into "coherent" (b=b') and "incoherent" ($b\neq b'$) contributions which are designated by σ^C and σ^I, respectively, such that

$$\sigma^C(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\mathcal{B}}\sum_{b}P_{\mathcal{B}b} \tag{2.9}$$

$$(x)\sum_{\alpha\alpha'}a^*_{\alpha bb}\,a_{\alpha' bb}\int d\tau\, e^{-i\omega\tau}\langle\mathcal{B}|e^{-i\underline{\kappa}\cdot\underline{R}_\alpha(0)}e^{i\underline{\kappa}\cdot\underline{R}_{\alpha'}(\tau)}|\mathcal{B}\rangle$$

and

$$\sigma^I(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)\sum_{\mathcal{B}}\sum_{b'b}P_{\mathcal{B}b} \tag{2.10}$$

$$(x)\sum_{\alpha\alpha'}a^*_{\alpha b'b}\,a_{\alpha' b'b}\int d\tau\, e^{i(\omega_{b'b}-\omega)\tau}\langle\mathcal{B}|e^{-i\underline{\kappa}\cdot\underline{R}_\alpha(0)}e^{i\underline{\kappa}\cdot\underline{R}_{\alpha'}(\tau)}|\mathcal{B}\rangle$$

The incoherent cross section may be simplified immediately. This cross section involves the product $a^*_{\alpha b'b}\,a_{\alpha' b'b}$. Writing out this product from Eq. (2.4), then employing the fact that the internal state functions factor into individual particle state functions as indicated in Eq. (1.25), one finds that for $b'\neq b$, $a^*_{\alpha b'b}\,a_{\alpha' b'b}$ vanishes unless $\alpha=\alpha'$. This result is obtained because of the orthogonality of the individual particle internal state functions. Therefore the incoherent cross section reduces to the form

$$\sigma^I(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\mathcal{B}}\sum_{b'b}P_{\mathcal{B}b} \tag{2.11}$$

$$(x)\sum_{\alpha}|a_{\alpha b'b}|^2\int d\tau\, e^{i(\omega_{b'b}-\omega)\tau}\langle\mathcal{B}|e^{-i\underline{\kappa}\cdot\underline{R}_\alpha(0)}e^{i\underline{\kappa}\cdot\underline{R}_\alpha(\tau)}|\mathcal{B}\rangle$$

The fact that $\alpha \neq \alpha'$ terms vanish in the incoherent cross section implies that it is not directly sensitive to the relative positions of the scattering particles. This conclusion was originally established by Breit.[63]

On the other hand, the $\alpha \neq \alpha'$ terms remain in the coherent scattering cross section and the resulting interference in coherent scattering may play a significant role, even in gases.

It is interesting to note that these conclusions do not depend on the preceeding approximations in this chapter, and in fact, one may establish them from the general expression for the cross section given by Eq. (1.59).

In order to develop a relationship between the scattering cross sections given by Eqs. (2.9) and (2.11) and particle correlation functions it would be convenient to average

$$\langle \mathcal{B} | e^{-i\underline{\kappa}\cdot\underline{R}_{\alpha}(0)} e^{i\underline{\kappa}\cdot\underline{R}_{\alpha'}(\tau)} | \mathcal{B} \rangle$$

over all external states. However, this averaging process is complicated by the fact that in general $P_{\mathcal{B}b}$ depends on both internal and external states in such a way that this dependence is not easy to separate. If one introduces the approximation

$$P_{\mathcal{B}b} = P_{\mathcal{B}} P_{b}$$

then the cross section as given by Eq. (2.8) becomes

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{b'b} P_b \tag{2.12}$$

$$(X) \sum_{\alpha\alpha'} a^*_{\alpha b'b}\, a_{\alpha' b'b} \int d\tau\, e^{i(\omega_{b'b}-\omega)\tau} \left\langle e^{-i\underline{K}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{K}\cdot\underline{R}_{\alpha'}(t+\tau)} \right\rangle$$

where

$$\left\langle e^{-i\underline{K}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{K}\cdot\underline{R}_{\alpha'}(\tau)} \right\rangle \equiv \sum_{\mathcal{B}} P_{\mathcal{B}} \langle \mathcal{B} | e^{-i\underline{K}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{K}\cdot\underline{R}_{\alpha'}(\tau)} | \mathcal{B} \rangle$$

For a system of particles of the same type all of which are initially in a nondegenerate ground state

$$P_{\mathcal{B}b} = P_{\mathcal{B}}\, \delta_{bb_0}$$

and the scattering cross section as given by Eq. (2.12) is appropriate with the sum over b restricted to the single term b_0. Initially <u>this</u> cross section will be developed in terms of correlation functions. Then the results will be extended to more complicated systems. To begin the development, following the method of Van Hove[49] it is convenient to introduce a Fourier transform of

$$\left\langle e^{-i\underline{K}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{K}\cdot\underline{R}_{\alpha'}(\tau)} \right\rangle$$

defined by

$$G_{\alpha\alpha'}(\underline{\rho},\tau) = (2\pi)^{-3} N^{-1} \int d^3K\, e^{-i\underline{K}\cdot\underline{\rho}} \left\langle e^{-i\underline{K}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{K}\cdot\underline{R}_{\alpha'}(\tau)} \right\rangle \tag{2.13}$$

$$= (2\pi)^{-6} N^{-1} \int d^3r\, d^3K\, d^3K' \left\langle e^{i\underline{K}\cdot[\underline{r} - \underline{R}_\alpha(0)]} \right.$$

$$\left. (X)\; e^{i\underline{K}'\cdot[\underline{r} + \underline{\rho} - R_{\alpha'}(\tau)]} \right\rangle$$

Integrating over $\underline{k}$ and $\underline{k}'$ one obtains

$$G_{\alpha\alpha'}(\underline{\rho},\tau) = N^{-1}\int d^3r \left\langle \delta[\underline{r}-\underline{R}_\alpha(0)]\,\delta[\underline{r}+\underline{\rho}-\underline{R}_{\alpha'}(\tau)]\right\rangle \tag{2.14}$$

The dependence of $G_{\alpha\alpha'}(\rho,\tau)$ on initial time is not indicated. The integral over r may not be performed directly because the arguments of the two δ-functions do not commute (except for $\tau=0$).

Inverse transformation of Eq. (2.13) yields

$$\left\langle e^{-i\underline{k}\cdot\underline{R}_\alpha(0)}\, e^{i\underline{k}\cdot\underline{R}_{\alpha'}(\tau)}\right\rangle = N\int d^3\rho\, e^{i\underline{k}\cdot\underline{\rho}}\, G_{\alpha\alpha'}(\underline{\rho},\tau) \tag{2.15}$$

If Eq. (2.15) is substituted into Eqs. (2.8), (2.9), and (2.11), the cross sections become

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\to\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{b'}\sum_{\alpha\alpha'}^{N} a^*_{\alpha b'b}\,a_{\alpha' b'b}\,S_{\alpha\alpha'}(\underline{k},\omega-\omega_{b'b}) \tag{2.16}$$

$$\sigma^{c}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\to\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\alpha\alpha'}^{N} a^*_{\alpha bb}\,a_{\alpha' bb}\,S_{\alpha\alpha'}(\underline{k},\omega) \tag{2.17}$$

$$\sigma^{I}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\to\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{b'}\sum_{\alpha}^{N} |a_{\alpha b'b}|^2\,S_{\alpha\alpha}(\underline{k},\omega-\omega_{b'b}) \tag{2.18}$$

when

$$S_{\alpha\alpha'}(\underline{k},\omega) \equiv \frac{1}{2\pi}\int d^3\rho\, d\tau\, e^{i(\underline{k}\cdot\underline{\rho}-\omega\tau)}\, G_{\alpha\alpha'}(\underline{\rho},\tau) \tag{2.19}$$

At times it will be useful to break up the coherent cross section into coherent direct ($\alpha=\alpha'$), and coherent interference ($\alpha\neq\alpha'$) contributions as follows:

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\to\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\alpha} |a_{\alpha b'b}|^2\,S_{\alpha\alpha}(\underline{k},\omega) \tag{2.20}$$

$$\sigma^{CN}(\epsilon_1\omega_1\Omega_1\rightarrow\epsilon_2\omega_2\Omega_2)=\frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\alpha\alpha'}a^*_{\alpha b'b}\,a_{\alpha' b'b}\,S_{\alpha\alpha'}(\underline{K},\omega) \tag{2.21}$$

For a system of like particles each initially in the same individual internal state $|\beta\rangle$

$$|a_{\alpha bb}|^2 = a_{\alpha bb}\,a_{\alpha' bb} = |a_{\beta\beta}|^2$$

and

$$\sum_{b'}{}'\,|a_{\alpha b'b}|^2 e^{i\omega_{b'b}\tau} = \sum_{\beta'\neq\beta}|a_{\beta'\beta}|^2 e^{i\omega_{\beta'\beta}\tau}$$

In analogy with Eqs. (2.3) and (2.4) (2.22)

$$a_{\beta'\beta} = Z(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\delta_{\beta'\beta}+\frac{1}{\hbar m}\sum_{\beta''}\left\{\frac{\langle\beta'|\Pi_2|\beta''\rangle\langle\beta''|\Pi_1|\beta\rangle}{\omega_1-\omega_{\beta''\beta}}-\frac{\langle\beta'|\Pi_1|\beta''\rangle\langle\beta''|\Pi_2|\beta\rangle}{\omega_2+\omega_{\beta''\beta}}\right\}$$

for molecules, and

$$a_{\beta'\beta} = \underline{\epsilon}_1\cdot\underline{\epsilon}_2\,\delta_{\beta'\beta} \tag{2.23}$$

for free electron.

Introducing these results into Eqs. (2.18), (2.20), and (2.21) and substituting for $S_{\alpha\alpha'}(\underline{\kappa},\omega)$ from Eq. (2.19), the cross sections become for a system of like particles each in the same initial state

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\epsilon_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2|a_{\beta\beta}|^2 \tag{2.24}$$

$$(\times)\int d^3\rho\,d\tau\,e^{i[\underline{K}\cdot\underline{\rho}-\omega\tau]}\,G^s(\underline{\rho},\tau)$$

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2|a_{\beta\beta}|^2 \tag{2.25}$$

$$(\times)\int d^3\rho\,d\tau\,e^{i[\underline{K}\cdot\underline{\rho}-\omega\tau]}\,G^P(\underline{\rho},\tau).$$

$$\sigma^{I}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\beta'}\left|a_{\beta'\beta}\right|^2 \tag{2.26}$$

$$(\times)\int d^3\rho\, d\tau\, e^{i\left[\underline{k}\cdot\underline{\rho}+(\omega_{\beta'\beta}-\omega)\tau\right]}G^S(\underline{\rho},\tau)$$

where

$$G^S(\underline{\rho},\tau)=\sum_{\alpha}G_{\alpha\alpha}(\underline{\rho},\tau) \tag{2.27}$$

and

$$G^P(\underline{\rho},\tau)=\sum_{\alpha\alpha'}{}'\,G_{\alpha\alpha'}(\underline{\rho},\tau) \tag{2.28}$$

The sum of these two functions is

$$G(\underline{\rho},\tau)=G^S(\underline{\rho},\tau)+G^P(\underline{\rho},\tau) \tag{2.29}$$

The superscripts S and P stand for "single" and "pair," respectively.

The functions G^S, G^P and G are identical to the G-functions introduced by Van Hove,[49] who describes in some detail the significance and behavior of these functions in various types of scattering systems. A few of their properties which are of immediate interest are discussed in the following paragraphs.

From Eq. (2.27) and the fact that $R_\alpha(t)$ and $R_{\alpha'}(t+\tau)$ commute for $\tau=0$,

$$G^S(\underline{\rho},0)=\delta(\underline{\rho}) \tag{2.30}$$

and

$$G^P(\underline{\rho},0)=g(\underline{\rho}) \tag{2.31}$$

where

$$g(\underline{\rho}) \equiv N^{-1}\sum_{\alpha\alpha'}{}' \left\langle \delta\left[\underline{R}_{\alpha}(0)+\underline{\rho}-\underline{R}_{\alpha'}(0)\right]\right\rangle \qquad (2.32)$$

The G-functions can be calculated directly for an ideal gas. These calculations are carried out in Appendix E. The results for particles in a Maxwellian distribution at a temperature T are

$$G^{S}_{IG}(\underline{\rho},\tau)= \left(\frac{M}{2\pi\tau^{2}\xi}\right)^{3/2} e^{-\frac{M\rho^{2}}{2\tau^{2}\xi}} \qquad (2.33)$$

and

$$G^{P}_{IG}(\underline{\rho},\tau) = \frac{N-1}{L^{3}} \qquad (2.34)$$

where in Eq. (2.33)

$$\xi = \Theta - \frac{i\hbar}{\tau} \qquad (2.35)$$

and Θ = kT where k in Boltzmann's constant.

Notice that ξ and therefore G^{S} are complex. Although the G-functions clearly depend on pairs of position coordinates and therefore contain effects of particle correlations, they do not seem to conform to a simple physical interpretation. Moveover, the calculation of these functions for realistic models of many physical systems has proven to be quite difficult. One popular recourse has been to replace the G-functions by corresponding classical limits which we denote by $\mathcal{G}^{S}(\rho,\tau)$, $\mathcal{G}^{P}(\underline{\rho},\tau)$ and $\mathcal{G}(\underline{\rho},\tau)$. A classical limit may be obtained from the quantum function simply by replacing the noncommuting operators $R_{\alpha}(0)$ and $R_{\alpha}(\tau)$ by their commuting classical counterparts, at the same time replacing the average over quantum states by a classical ensemble average. This is the so-called Vineyard perscription.[64]

Rosenbaum and Zweifel[65] have examined the validity of the Vineyard perscription for scattering cross sections. They find that the dominant correction to the cross section is given by the factor

$$e^{\frac{\epsilon}{2\Theta}}\, e^{-\frac{(\Delta p)^2}{8M\Theta}}$$

where ϵ is the energy transfer to external states, M, the mass of the scattering particles, and Δp, the momentum transfer during a scattering transition. For neutron scattering this factor is significant under appropriate conditions (high incident energy, large momentum transfers, and scattering particles of small mass). On the other hand, for light scattering the momentum transfer $\hbar k$ and energy transfer $\hbar\omega$ to external states are extremely small in comparison, and this correction is very small except near absolute zero.

Thus it appears that the classical limits of the G-functions are adequate for light scattering cross sections. This conclusion is supported by a direct comparison of the quantum scattering cross section for the ideal gas (which can be calculated rigorously) and the corresponding classical cross section obtained using the Vineyard perscription. Such a comparison is developed in Appendix E.

One obtains for the classical limit of $G(\underline{\rho}, \tau)$

$$\mathcal{G}(\underline{\rho},\tau) = \sum_{\alpha\alpha'} \left\langle \delta[\underline{R}_\alpha(0) + \underline{\rho} - \underline{R}_{\alpha'}(t+\tau) \right\rangle \tag{2.36}$$

Corresponding results are obtained for $\mathcal{G}^S(\rho,\tau)$ and $\mathcal{G}^P(\rho,\tau)$. In scattering systems whose statistical properties do not vary over space, these classical limits possess simple physical interpretations; i.e.,

$\mathcal{G}(\rho_-,\tau)d^3\rho$ = the conditional probability, given that there is a particle at $\underline{r}$ at time 0, that there is a particle in $d^3\rho$ at $\underline{r} + \rho_-$ at time τ.

$\mathcal{G}^S(\rho_-,\tau)d^3\rho$ = the conditional probability, given that there is a particle at $\underline{r}$ at time 0, that the <u>same</u> particle is in $d^3\rho_-$ at time τ.

$\mathcal{G}^P(\rho_-,\tau)d^3\rho$ = the conditional probability, given that there is a particle at $\underline{r}$ at time 0, that a <u>different</u> particle is in $d^3\rho$ at $\underline{r} + \rho_-$ at time τ.

The classical limit of $g(\rho_-)$ is also of interest. This limit is obtained simply by replacing the quantum average in Eq. (2.32) by a classical average. Both the quantum and classical functions have the physical interpretation

$g(\rho)d^3\rho$ = the conditional probability, given that there is a particle at $\underline{r}$, that simultaneously there is a particle in $d^3\rho$ at $\underline{r} + \rho_-$.

The results obtained so far apply to a system of like particles, each of which is in the same initial state. These results may be extended directly to a system containing several different types of particles, each of which is in a nondegenerate ground state. The cross section given by Eq. (2.12) is still appropriate. Breaking up the sums over α and α' into M sums apiece, one for each type of particle, one obtains

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{b'} \sum_{\mu\mu'}^{M} \sum_{\alpha}^{N_\mu} \sum_{\alpha'}^{N_{\mu'}} a^*_{\alpha b'b}\, a_{\alpha' b' b} \tag{2.37}$$

$$(x) \int d^3\rho\, d\tau\, e^{i[\underline{k}\cdot\underline{\rho} + (\omega_{b'b} - \omega)\tau]}\, G_{\alpha\alpha'}(\underline{\rho},\tau)$$

Here N_μ and $N_{\mu'}$ are the numbers of particles of type μ and μ', respectively. Since all particles of a given type are in the same initial state, we have

$$\sum_{b'} \sum_{\alpha}^{N_\mu} \sum_{\alpha'}^{N_{\mu'}} a^*_{\alpha b' b}\, a_{\alpha' b' b}\, e^{i\omega_{b'b}\tau} G_{\alpha\alpha'}(\underline{\rho},\tau) = \sum_{b'} a^*_{\mu b' b}\, a_{\mu' b' b}\, e^{i\omega_{b'b}\tau} \sum_{\alpha}^{N_\mu} \sum_{\alpha'}^{N_{\mu'}} G_{\alpha\alpha'}(\underline{\rho},\tau)$$

The subscripts μ and μ' on $a^*_{\mu b'b}$ and $a_{\mu' b' b}$ denote arbitrary particles of type μ and μ', respectively. Substituting this result into Eq. (2.37), the cross section becomes

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{b'} \sum_{\mu\mu'}^{M} a^*_{\mu b' b}\, a_{\mu' b' b} \tag{2.38}$$

$$(x) \int d^3\rho\, d\tau\, e^{i[\underline{k}\cdot\underline{\rho} + (\omega_{b'b} - \omega)\tau]} \sum_{\alpha}^{N_\mu} \sum_{\alpha'}^{N_{\mu'}} G_{\alpha\alpha'}(\underline{\rho},\tau)$$

Finally, breaking up this cross section into coherent direct, coherent interference, and incoherent cross sections, one obtains

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta} P_\beta |a_{\beta\beta}|^2 \int d^3\rho\, d\tau\, e^{i(\underline{k}\cdot\underline{\rho} - \omega\tau)} G^S_\beta(\underline{\rho},\tau) \tag{2.39}$$

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta\beta'} P_\beta\, a^*_{\beta\beta}\, a_{\beta'\beta'} \tag{2.40}$$

$$(x) \int d^3\rho\, d\tau\, e^{i[\underline{k}\cdot\underline{\rho} - \omega\tau]} G^P_{\beta\beta'}(\underline{\rho},\tau)$$

$$\sigma^{I}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta\beta'} P_\beta\, |a_{\beta'\beta}|^2 \tag{2.41}$$

$$(x) \int d^3\rho\, d\tau\, e^{i[\underline{k}\cdot\underline{\rho} + (\omega_{\beta'\beta} - \omega)\tau]} G^S_\beta(\underline{\rho},\tau)$$

Here

$$P_\beta = \frac{N_\beta}{N}$$

In these equations β designates both the type of particle and a particular initial state. In Eq. (2.40) β' also designates both a type of particle and its initial state, whereas in Eq. (2.41) β' designates an appropriate final state. Of course so far the initial states are restricted to nondegenerate ground states. The functions

$$G^S_\beta(\rho,\tau) = \frac{N}{N_\beta}\sum_{\alpha}^{N_\beta} G_{\alpha\alpha}(\rho,\tau) \tag{2.42}$$

$$G^P_{\beta\beta'}(\rho,\tau) = \frac{N}{N_\beta}\sum_{\alpha}^{N_\beta}\sum_{\alpha'}^{N_{\beta'}}{}' G_{\alpha\alpha'}(\rho,\tau) \tag{2.43}$$

have been introduced. The prime on the sum over β' implies that if $\beta = \beta'$, the term for which $\alpha = \alpha'$ is to be excluded.

We denote the classical limits of G^S_β and $G^P_{\beta\beta'}$ by $\mathcal{G}^S_\beta$ and $\mathcal{G}^P_{\beta\beta'}$. These classical limits may be obtained from their quantum counterparts in the same manner employed to obtain $\mathcal{G}^S$ and $\mathcal{G}^P$. In a system whose statistical properties do not vary over space they have the physical interpretations

$\mathcal{G}^S_\beta(\rho,\tau)d^3\rho$ ≡ conditional probability, given that a particle of type β is at possition $\underline{r}$ at time 0, that the same particle will be in $d^3\rho$ at $\underline{r} + \underline{\rho}$ at time τ.

$\mathcal{G}^P_{\beta\beta'}(\underline{\rho},\tau)d^3\rho$ = conditional probability, given that a particle of type β is at position r at time 0, that a different particle of type β' will be in $d^3\rho$ at $\underline{r} + \underline{\rho}$ at time τ.

Note that β may equal β' in $\mathcal{G}^P_{\beta\beta'}(\underline{\rho},\tau)$.

To a certain approximation Eqs. (2.39), (2.40), and (2.41) may be applied to systems of particles in various initial internal states by treating particles of the same kind but in different initial internal states as different types of particles. In this approximation the effect on correlations of particle transitions from one internal state to another is neglected. If the distribution of particles about each other does not depend sensitively on the initial states of the particles, then this approximation ought to be good. Otherwise it may still be an acceptable first approximation. In subsequent work this approximation will be adopted wherever necessary. However it is discussed again in Section 2.5.

As mentioned previously, the light scattered from a monochromatic incident beam will be concentrated, typically, into a number of sharp spectral lines. Of course these lines may overlap, or appear to do so because of the limited resolution of an experiment. For coherent scattering $\omega_{b'b} = 0$ and, as a result, the corresponding line will be centered on or very near the incident line at ω_1. On the other hand, lines arising from incoherent scattering may be centered on or very near ω_1, if $\omega_{b'b} = 0$ (states b and b' members of the same level), or shifted up or down in frequency if $\omega_{b'b} \neq 0$. Thus a particular line will correspond to an internal state transition from an initial level

B to a final level B'.* In order to calculate the incoherent cross section for a particular line it is only necessary to sum over those states β and β' in the corresponding levels B and B'. We denote this restricted sum by $\sum_{\beta}^{B} \sum_{\beta'}^{B'}$ and the corresponding cross section by

$$\sigma^{B'\to B}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta}^{B} P_\beta {\sum_{\beta'}^{B'}}' |a_{\beta'\beta}|^2$$

$$(\mathrm{x}) \int d^3\rho \, d\tau \, e^{i[\underline{K}\cdot\underline{\rho} + (\omega_{B'B} - \omega)\tau]} G^S(\underline{\rho},\tau) \qquad (2.44)$$

It may be that several different sets of levels have the same energy difference, in which case $\sigma^{B\to B'}$ must be summed over those sets in order to obtain the cross section for the observed line. A particular example of this situation arises for incoherent Rayleigh scattering; the corresponding cross section is given by

$$\sigma^{I\,Ray}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \sum_{B} \sigma^{B\to B}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) \qquad (2.45)$$

Because of the prime on the sum over β' in Eq. (2.44), only degenerate levels contribute to σ^{IRay}. Thus this cross section would not be significant for argon gas at STP because nearly all the atoms are in nondegenerate ground states.

The scattering of light from free electrons is often called Thomson scattering. It is convenient for present purposes to apply the term

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*Here we define a level to include all states within a small energy range corresponding to the resolution of the contemplated experiment.

Rayleigh scattering to that for which $\omega_{b'b} = 0$. We refer to Raman scattering as that for which $\omega_{b'b} \neq 0$. Under these conventions the coherent cross section contains the Thomson scattering and coherent Rayleigh scattering whereas the incoherent cross sections contain Raman scattering and any incoherent Rayleigh scattering that may arise.

In Sections 2.2 and 2.3 the results of this section are used to discuss the coherent and incoherent cross sections in more detail.

2.2. THE COHERENT SCATTERING CROSS SECTION

It is convenient to consider first the behavior of the coherent scattering cross section in an ideal gas. We assume for simplicity that the scattering system is composed of identical particles in a nondegenerate ground state. Substituting from Eqs. (E.29) and (E.30) for the Fourier transforms of classical limits of the G-functions in an ideal gas, one obtains from Eqs. (2.39) and (2.40)

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \left|a_{\beta\beta}\right|^2 \left(\frac{M}{2\pi\Theta\kappa^2}\right)^{1/2} e^{-\frac{M\omega^2}{2\Theta\kappa^2}} \tag{2.46}$$

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \left|a_{\beta\beta}\right|^2 \frac{N-1}{L^3}(2\pi)^2\delta(\underline{k})\delta(\omega) \tag{2.47}$$

Because of the δ-functions $\delta(\underline{k})\ \delta(\omega)$ which appear in Eq. (2.47), interference scattering in an ideal gas is indistinguishable from the incident beam and thus unobservable in a scattering experiment. This result is consistent with the well known conclusion first established by Lord Rayleigh[4,5] that the light scattered from the particles of an ideal gas may be regarded as the sum of the light scattered from each particle.

We turn now to a consideration of coherent scattering in a real gas. In this case it is not clear that interference scattering may be ignored, particularly if one is interested in the frequency distribution of the scattered light in a particular spectral line. As implied previously, in gases near STP observation of the detailed shape of a line would require resolution of better than 0.01 angstrom. Admittedly, using conventional experimental techniques it would be difficult to attain such resolution because of the problems involved in obtaining a sufficiently intense and monochromatic incident beam as well as problems concerning spectrographic resolution which are especially severe at the low light intensities characteristic of scattering experiments. However, appropriate laser light sources will provide intense, sufficiently monochromatic light beams. Using such sources, it appears likely that high resolution techniques such as those employing a Fabry Perot etalon[66] or optical heterodyne techniques[67] may allow the observation of detailed line shapes in light scattering from gases.

With such experiments in mind it appears worthwhile to consider the frequency dependence of the coherently scattered light from a real gas, including both direct and interference scattering contributions. In our formulation this frequency dependence depends upon $\mathcal{G}(\rho_-,\tau)$. "Semi-quantitative estimates" of this function and its transform in argon gas at atmospheric pressure and 0°C have been calculated by Nelkin and Yip,[68] whose results indicate that the frequency dependence of the scattered light should be considerably different from that resulting from the ideal gas assumption. Similar results were obtained for a gas by Landau and Placzek[22] in 1934 from classical fluctuation theory. The present approach appears to offer the advantage of a more detailed analysis. Recently, considerable interest seems to be developing in this approach.[69]

The detail in the frequency spectrum reflects the differences between $\mathcal{G}(\rho_-,\tau)$ and $\mathcal{G}_{IG}(\rho_-,\tau)$ which arise because of the interactions between particles which are present in the real gas. However, the effect of these interactions on the frequency spectrum is not contained entirely in $\mathcal{G}(\rho_-,\tau)$. That part of the particle-particle interactions represented by V^I (see Eqs. (1.19) and (1.20)) may give rise to pressure broadening of initial, intermediate, and final states. Away from resonance the widths of the intermediate states do not play a significant role. Furthermore, it is argued in Appendix B that the widths of initial and final states should affect the cross section through their difference. Since the initial and final internal states are the same, and the external and radiation states change only slightly, the initial and final widths should be nearly equal and their effect should be small.

However, the perturbation V^I also affects the cross section through the matrix elements V^IV^2 and V^2V^I which occur in the numerators of the second-order term, and through matrix products $V^2V^IV^I$, $V^IV^2V^I$, $V^IV^IV^2$, $V^1V^1V^I$, $V^1V^IV^1$, and $V^IV^1V^1$ in the third-order terms which have not been considered previously. These contributions are discussed briefly in Section 2.5. In particular, it appears that the matrix element product $V^1V^IV^1$ may introduce a broadening of the spectral distribution which could obscure the detail contributed by $\mathcal{G}(\rho_-,\tau)$ under certain conditions.

Very near the critical point in a gas the isothermal compressibility (dV/dP) grows large. As a result there is very little "restoring force" for density fluctuations within the gas and these fluctuations grow large, displaying strong correlation. Under this circumstance, coherent interference scattering can dominate the scattering cross section which increases by many orders of magnitude to the point where the scattering becomes clearly visible to the naked eye. This phenomenon is known as critical scattering or critical opalescence. The classical theory of critical scattering was developed by Ornstein and Zernicke[19] with contributions from Placzek,[70] and others. Early experimental observations of critical scattering are discussed by Cabannes.[24] Fixman[71] presents a recent (1964) summary of the theory of the critical state, and devotes some attention to critical scattering experiments. These experiments have been performed on gases and liquid mixtures (in which concentration fluctuations instead of density fluctuations generate the critical scattering). They usually involve measurements of the angular distribution of the scattered light, which differs considerably from that of noncritical scattering. It is interesting to note from Fixman's remarks that the present theory of critical scattering and corresponding experimental results do not always agree satisfactorily.

We shall not discuss the phenomenon of critical scattering in detail here, but wish to point out the relevance of the G-function formalism and the possible interest of measurements of the frequency distribution of light scattered from a monochromatic beam passing through a system near the critical state. Such experiments have apparently not been reported yet.

2.3. THE INCOHERENT SCATTERING CROSS SECTION

Incoherent Rayleigh scattering is observed when a significant number of particles in the scattering system are in initial levels containing two or more states. One example of such a system is cesium vapor, which at several hundred degrees centigrade is composed predominantly of single atoms in ground states which are twofold degenerate because of the electron spin of 1/2. Another example is a polyatomic gas, where several types of true degeneracy may be present in addition to closely spaced rotational states, which, if they cannot be resolved, are included in the present definition of a level. In Section 4.2 it is shown that among other things, incoherent scattering accounts for depolarization of light Rayleigh-scattered through 90°, an important phenomenon as it reveals considerable information about the structure of the scattering particles.

For the incoherent Rayleigh scattering, one obtains from Eqs. (2.44) and (2.45)

$$\sigma^{I\,Ray}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{B} \sum_{\beta\beta'}^{B}{}' P_\beta \left| a_{\beta'\beta} \right|^2 \qquad (2.48)$$
$$(x) \int d^3\rho\, d\tau\, e^{i[\underline{k}\cdot\underline{\rho} - \omega\tau]}\, G_\beta^S(\underline{\rho},\tau)$$

In the ideal gas approximation, assuming a Maxwellian distribution at a temperature T and, for simplicity, like particles in nondegenerate ground states, substituting for S^S from Eq. (E.30) one obtains

$$\sigma^{I\,Ray}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta'}^{B} \left| a_{\beta'\beta} \right|^2 \qquad (2.49)$$
$$(x) \left(\frac{M}{2\pi\Theta K^2}\right)^{1/2} e^{-\frac{M\omega^2}{2\Theta K^2}}$$

The cross section for the Raman scattering line corresponding to the transition from level B to level B' is given by Eq. (2.44). Again in the ideal gas approximation, under the same assumptions leading to Eq. (2.49) one obtains

$$\sigma^{B\rightarrow B'}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta'}^{B'}{}' \left| a_{\beta'\beta} \right|^2$$
$$(x) \left(\frac{M}{2\pi\Theta K^2}\right)^{1/2} e^{-\frac{M}{2\Theta K^2}(\omega - \omega_{B'B})^2}$$

It is interesting to note that the detailed shape of an <u>incoherent</u> scattering line is related to $\mathcal{G}_\beta^S$ instead of $\mathcal{G}_\beta$. In an experiment which observes light Rayleigh-scattered through 90°, that part of the light which is polarized parallel to the plane of scattering arises entirely from incoherent scattering whereas in a typical situation the light polarized perpendicular to the plane of scattering will arise predominantly from coherent scattering.* Since the latter is related to $\mathcal{G}$ and the former to $\mathcal{G}^S$, it is conceivable and appears likely that the Rayleigh line shape may depend significantly on the polarization observed at the detector.

2.4. THE CROSS SECTION FOR A PARTICULAR RAYLEIGH OR RAMAN LINE, INTEGRATED OVER ω_2

Up to this point in Chapter II, cross sections which describe the detailed shapes of spectral lines of light scattered from a monoenergetic incident beam in gases have been developed and examined. However, as pointed out previously, observation of this detail is extremely difficult, lying near the limit of prelaser capabilities. Apparently the most detailed quantity measured carefully to date (in gas scattering experiments) is the intensity of lines integrated over frequency as a function of polarization or angle of scattering. From Eq. (1.57), for the line corresponding to the transition from level B to level B' we have for the integrated intensity

$$I_S^{B\to B'}(R\,|\,\underline{\epsilon}_2\underline{\Omega}_2) = \frac{V_s N_0}{R^2}\sum_\lambda \int d\omega_1\, d\Omega_1\, I(\underline{\epsilon}_\lambda \omega_\lambda \underline{\Omega}_1) \tag{2.51}$$
$$(X) \int d\omega_2 \frac{\omega_2}{\omega_1}\, \sigma^{B\to B'}(\underline{\epsilon}_\lambda \omega_1 \underline{\Omega}_1 \to \underline{\epsilon}_2 \omega_2 \underline{\Omega}_2)$$

Substituting from Eq. (2.44) for $\sigma^{B\to B'}$, this equation becomes

$$I_S^{B\to B'}(R\,|\,\underline{\epsilon}_2\underline{\Omega}_2) = \frac{V_s N_0}{R^2}\,\frac{1}{2\pi}\left(\frac{e^2}{mc^2}\right)^2 \sum_\lambda \int d\omega_1\, d\Omega_1\, I(\underline{\epsilon}_\lambda \omega_1 \underline{\Omega}_1) \tag{2.52}$$

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*These statements are justified in Chapter IV.

$$(x)\int d\omega_2\left(\frac{\omega_2}{\omega_1}\right)^2\sum_{\beta}^{B}P_\beta\sum_{\beta'}^{B'}\left|a_{\beta'\beta}\right|^2\int d^3\rho\, d\tau\, e^{i[\underline{\kappa}\cdot\underline{\rho}+(\omega_{B'B}-\omega)\tau}G_\beta^s(\rho,\tau) \quad (2.52)$$

For the intensity corresponding to coherent direct, coherent interference or incoherent Rayleigh scattering the cross section $\sigma^{B\to B'}$, in Eq. (2.51) should be replaced by σ^{CD}, σ^{CN}, or σ^{IRay}, respectively.

The cross sections integrated over ω_2 retain considerable information about the scattering particles, and probably will remain important experimentally and theoretically even as refined laser scattering techniques are developed. These cross sections can be expressed in terms of one-time correlation functions through the so-called static approximation which is well known in neutron and x-ray scattering theory. These correlation functions are easier to calculate and interpret than the Van Hove G-functions.

Perhaps the simplest development of the static approximation involves an approximate integration over ω_2 in Eq. (2.52). The integrand depends on ω_2 through the ration $(\omega_2/\omega_1)^2$, through the quantities $|a_{\beta'\beta}|^2$ and through $\underline{\kappa}$ and ω. However, the variation of all these quantities except ω over a typically sharp line is usually negligible. Thus it appears that to a good approximation one may evaluate $(\omega_2/\omega_1)^2$, $|a_{\beta'\beta}|^2$ and $\underline{\kappa}$ at the line center, for which $\omega_2 \cong \omega_1-\omega_{b'b}$. Moreover, because of the sharpness of the line, to a good approximation the lower limit of the integral over ω_2 may be extended to $-\infty$. Under these approximations the integration acts only on $e^{i\omega\tau}$, yielding $2\pi\delta(\tau)$. Then the integral over τ may be performed directly, and one obtains

$$I_S^{B\to B'}(\underline{R},\underline{\epsilon}_2\underline{\Omega}_2) = \frac{V_S N_0}{R^2}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\lambda}\int d\omega_1 d\Omega_1\, I(\underline{\epsilon}_\lambda \omega_1 \underline{\Omega}_1) \tag{2.52}$$

$$(\times)\left(\frac{\omega_1-\omega_{B'B}}{\omega_1}\right)^2 \sum_{\beta}^{B} P_\beta \sum_{\beta'}^{B'} |a_{\beta'\beta}|^2 \int d^3\rho\, e^{i\underline{K}_{B'B}\cdot\underline{\rho}}\, G_\beta^S(\underline{\rho},0)$$

where

$$\underline{K}_{B'B} = \underline{K}_0 + \frac{\omega_{B'B}}{c}\underline{\Omega}_2$$

and

$$\underline{K}_0 = \frac{\omega_1}{c}(\underline{\Omega}_1 - \underline{\Omega}_2)$$

It is convenient to define

$$\sigma^{B\to B'}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \frac{\omega_1-\omega_{B'B}}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta}^{B} P_\beta \sum_{\beta'}^{B'} |a_{\beta'\beta}|^2 \int d^3\rho\, e^{i\underline{K}_{B'B}\cdot\underline{\rho}}\, G_\beta^S(\underline{\rho},0) \tag{2.53}$$

and likewise for the coherent direct, coherent interference, and incoherent Rayleigh cross sections

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta} P_\beta |a_{\beta'\beta}|^2 \int d^3\rho\, e^{i\underline{K}_0\cdot\underline{\rho}}\, G_\beta^S(\underline{\rho},0) \tag{2.54}$$

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta} P_\beta\, a^*_{\beta\beta}\, a_{\beta'\beta'} \int d^3\rho\, e^{i\underline{K}_0\cdot\underline{\rho}}\, G_{\beta\beta'}^P(\underline{\rho},0) \tag{2.55}$$

$$\sigma^{IRay}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \sum_{B} \sum_{\beta\beta'}^{B}{}' P_\beta |a_{\beta'\beta}|^2 \int d^3\rho\, e^{i\underline{K}_0\cdot\underline{\rho}}\, G_\beta^S(\underline{\rho},0) \tag{2.56}$$

From Eqs. (2.42) and (2.14),

$$G_\beta^S(\underline{\rho},0) = \delta(\underline{\rho}) \tag{2.57}$$

From Eqs. (2.43) and (2.14),

$$G_{\beta\beta'}^P(\underline{\rho},0) = \frac{1}{N_\beta}\sum_{\alpha}^{N_\beta}\sum_{\alpha'}^{N_{\beta'}} \langle \delta[\underline{R}_\alpha(0) + \underline{\rho} - \underline{R}_{\alpha'}(\tau)]\rangle \tag{2.58}$$

Consistent with Eq. (2.32), we define

$$g_{\beta\beta'}(\underline{\rho}) \equiv G^{P}_{\beta\beta'}(\underline{\rho}, 0) \tag{2.59}$$

Then $g_{\beta\beta'}$ has the physical interpretation (in a system whose statistical properties do no vary over space)

$g_{\beta\beta'}(\rho)d^3\rho^{*}$ ≡ the conditional probability, given that there is a partical of type β at $\underline{r}$ at time t, that simultaneously there will be a particle of type β' in $d^3\rho$ about $\underline{r} + \underline{\rho}$.

Substituting Eqs. (2.57) and (2.59) into Eqs. (2.53), (2.54), (2.55), and (2.56), one obtains:

$$\sigma^{B\to B'}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \frac{\omega_1 - \omega_{B'B}}{\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta}^{B} P_{\beta} \sum_{\beta'}^{B'} |a_{\beta'\beta}|^2 \tag{2.60}$$

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \sum_{\beta} P_{\beta} |a_{\beta\beta}|^2 \tag{2.61}$$

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 {\sum_{\beta\beta'}}' P_{\beta}\, a^{*}_{\beta\beta}\, a_{\beta'\beta'} \tag{2.62}$$

$$(\times) \int d^3\rho\, e^{i\underline{K}_0\cdot\underline{\rho}}\, g_{\beta\beta'}(\underline{\rho})$$

$$\sigma^{I\,Ray}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 \sum_{B} {\sum_{\beta\beta'}^{B}}' P_{\beta} |a_{\beta'B}|^2 \tag{2.63}$$

In the static approximation, the intensity integrated over a spectral line corresponding to a particular type of scattering may then be obtained from the equation

$$I(\underline{R}, \underline{\epsilon}_2\underline{\Omega}_2) = \frac{V_s N_0}{R^2} \sum_{\lambda} \int d\omega_1\, d\underline{\Omega}_1\, I(\underline{\epsilon}_\lambda \omega_1 \underline{\Omega}_1) \frac{\omega_2}{\omega_1} \sigma(\underline{\epsilon}_\lambda \omega_1 \Omega_1 \to \underline{\epsilon}_2\underline{\Omega}_2) \tag{2.64}$$

where the appropriate cross section, as given by Eqs. (2.60), (2.61)

(2.62), or (2.63) is to be inserted, and ω_2/ω_1 evaluated at the line center.

These results are well known. It has been shown here merely that they follow from the quantum expressions for the cross sections away from resonance in the static approximation. At least to the extent that the static approximation is valid, the dependence of these cross sections on internal and external states is separated (except for effects arising from line widths and higher order terms in the perturbation expansion here neglected).

Explicit correction terms to the static approximation can be developed by expanding the quantities which were evaluated at line centers in power series in ω. Or, one may employ the approach introduced by Placzek[72] with regard to neutron and x-ray scattering, in which the static approximation appears as the first contribution in the expansion of the cross section in terms of quantities which are closely related to moments of the energy distribution of the scattered particles or radiation about the line center.

Using either approach the first few correction terms in the ideal gas are extremely small. It does not seem likely that these corrections will be significant in a real gas or plasma except, perhaps, in the rare circumstance in which

$$S(\underline{\kappa},\omega) = \int d^3\rho\, d\tau\, e^{i[\underline{\kappa}\cdot\underline{\rho}-\omega\tau]}\, G(\underline{\rho},\tau) \qquad (2.65)$$

is sensitive to small variations in $\underline{\kappa}$ such as those which occur as ω passes through the spectral range $\Delta\omega$ over which a line is significant.

It is possible to present a fairly convincing argument that interference scattering will be insignificant in a real gas of atoms or simple molecules well away from a critical point. In order to keep the notation simple we will consider a system of like particles in nondegenerate ground states. Then Eq. (2.62) becomes

$$\sigma^{CN}(\epsilon_1\omega_1\Omega_1 \to \epsilon_2\Omega_2) = \left(\frac{e^2}{mc^2}\right)^2 \left|a_{\beta\beta}\right|^2 \int d^3\rho\, e^{i\underline{K}_0\cdot\underline{\rho}}\, g(\underline{\rho}) \tag{2.66}$$

In the ideal gas approximation, from Eqs. (2.31) and (2.34)

$$g_{IG}(\underline{\rho}) = \frac{N-1}{L^3} \tag{2.67}$$

and for this case the Fourier integral over $\underline{\rho}$ yields $(N-1)/L^3(2\pi)^3\delta(\underline{\kappa})$ which corresponds to unobservable forward scattering. It is convenient to define

$$g_1(\underline{\rho}) = g(\underline{\rho}) - g_{IG}(\underline{\rho}) \tag{2.68}$$

Since the integrals of $g(\underline{\rho})$ and $g_{IG}(\underline{\rho})$ over all $\underline{\rho}$ both equal N-1, we have

$$\int d^3\rho\, g_1(\underline{\rho}) = 0 \tag{2.69}$$

Also, from Eq. (2.32)

$$g_1(\underline{\rho}) = g_1(-\underline{\rho}) \tag{2.70}$$

Since $g_{IG}(\rho_-)$ does not contribute to observable scattering, for any observable contribution to Σ^{CN} one may replace $g(\rho_-)$ in Eq. (2.66) by $g_1(\rho_-)$, obtaining

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\underline{\Omega}_2) = \left(\frac{e^2}{mc^2}\right)^2 |a_{\beta\beta}|^2 \int d^3\rho\, e^{i\underline{\kappa}_0\cdot\underline{\rho}}\, g_1(\underline{\rho}) \qquad (2.71)$$

We seek a maximum value for the integral

$$I = \int d^3\rho\, e^{i\underline{\kappa}_0\cdot\underline{\rho}}\, g_1(\underline{\rho}) \qquad (2.72)$$

Noting from Eq. (2.70) that $g_1(\rho_-)$ is an even function of ρ_- the integral becomes

$$I = \int d^3\rho\, \cos(\underline{\kappa}_0\cdot\underline{\rho})\, g_1(\underline{\rho}) \qquad (2.73)$$

Expanding $\cos(\underline{\kappa}_0\cdot\rho_-)$ in a power series, the leading contribution to vanishes because of Eq. (2.69), and one obtains

$$I = \sum_{j=1}^{\infty} \frac{(-1)^j}{(2j)!} \int d^3\rho\, (\underline{\kappa}_0\cdot\underline{\rho})^{2j}\, g_1(\underline{\rho}) \qquad (2.74)$$

An upper limit for the value of this integral is given by

$$I_{max} = \sum_{j=1}^{\infty} \frac{1}{(2j)!} \int d^3\rho\, (\underline{\kappa}_0\cdot\underline{\rho})^{2j}\, |g_1(\underline{\rho})| \qquad (2.75)$$

In gases under conditions not near a critical point correlations between particles seem to persist only over very short distances comparable to particle dimensions. We assume that these distances may be characterized by a correlation range R such that the absolute value of $g_1(\rho_-)$ lies within the envelope

$$|g_1(\rho)|_{max} = N_0 e^{-\rho/R} \tag{2.76}$$

Substituting this expression for $|g_1(\rho_-)|$ in Eq. (2.75) and integrating over ρ_-, one obtains

$$I_{max} \leq 4\pi R^3 N_0 \sum_{j=1}^{\infty} (\kappa_0 R)^{2j} (2j+1) \tag{2.77}$$

This series converges if $\kappa_0 R < 1$. For light scattering κ_0 is of order 10^5 cm^{-1}(6000Å), whereas in gases of atoms or simple molecules we assume $R \cong 10^{-7}$ cm. At STP $N_0 \cong 3 \times 10^{19}$ cm^{-3}. For these values the series is dominated by the first term and

$$I_{max} \cong 10^{-5}$$

From Eqs. (2.61) and (2.62) this integral is the ratio

$$\frac{\sigma^{CN}(\epsilon_1 \omega_1 \underline{\Omega}_1 \rightarrow \epsilon_2 \underline{\Omega}_2)}{\sigma^{CD}(\epsilon_1 \omega_1 \underline{\Omega}_1 \rightarrow \epsilon_2 \underline{\Omega}_2)}$$

for a scattering system containing particles all in the same initial state. Similar results can be obtained under equivalent conditions for scattering systems containing more than one type of particle. Therefore we conclude that as far as the scattering integrated over a spectral line is concerned, the coherent interference contribution should not be significant in comparison to the coherent direct contribution in gases of atoms or simple molecules away from critical point.

2.5. FURTHER CONSIDERATION OF THE RELATIONSHIP BETWEEN SCATTERING CROSS SECTIONS AND THE VAN HOVE G-FUNCTIONS

In Section 2.1 we have expressed nonresonance light scattering cross sections in terms of correlation functions of particle positions in a model system whose particle-particle interactions are discribed by the Hamiltonian H^x. Thus the model system is one whose interparticle interactions depend only on the center-of-mass positions of the particles. We have been able to take into account part of the effect on particle correlations of the internal states of particles in the scattering system by treating particles in different states as particles of different types. However, it is implied in this treatment that the particles in the model system have been and will be in their initial states for all time. Thus we have neglected the effect of internal state transition on the position correlations. If internal state transitions affect the distribution of particles about each other over ranges and times which are significant for light scattering, the expression of the light scattering cross sections in terms of Van Hove G-functions as developed in Section 2.1 is subject to question.

At least part of the effect of internal state transitions may be contained in terms of the perturbation theory which have not been considered in Chapter II up to this point. For example, one may regard the matrix element products V^2V^I and V^IV^2 as matrix elements of V^2 between initial and final states which are partially corrected for collisional transitions. Third-order terms of the form $V^2V^IV^I$, $V^IV^2V^I$, $V^2V^2V^I$, $V^1V^1V^I$, and $V^IV^1V^1$ may be regarded similarly. These corrections might be incorporated into a more detailed definition of the G-functions in terms of corrected external state functions. It probably would be extremely difficult to calculate such functions with contemporary techniques; rather the present significance of this suggestion is that internal state transitions should be considered in calculating classical limits of the G-functions. For example, the effect of inelastic collisions might be considered in calculating correlations between electrons and ions.

It appears that these contributions will be small for systems of particles with nondegenerate ground states whose separation from first excited states is large compared to the kinetic energy per particle. Again, noble gases at temperatures up to several thousand degrees Kelvin form good examples of such systems. In systems of particles with degenerate or close lying initial states, it is more likely that these correction terms may be significant.

Matrix element products of the form $V^1V^IV^1$ apparently cannot be regarded as products of matrix elements of the form V^1V^1 between corrected initial and final states; rather they seem to pertain to the interaction of the scattering particles in intermediate states with the rest of the particle system. From elementary considerations[52] it appears that these transitions may contribute a broadening of the lines of scattered radiation. For example, Loudon[73] considers matrix elements of this type to account for energy exchanges between photons and phonons in a crystal during scattering interactions.

These conjectures will not be pursued further, because they lie beyond the scope of the second-order perturbation theory to which this dissertation has been confined. However, it may be necessary to consider the possible significance of these terms, particularly in such sensitive experiments as those mentioned in Section 2.2.

It is evident from Appendix D that in gases at separations from resonance comparable to $v/c\ \omega_1$, the description of scattering cross sections in terms of Van Hove G-functions fails. This result may be illustrated by a simple calculation under the ideal gas assumption. We shall not pursue this subject further here because of the many other considerations which must enter a careful treatment of resonance scattering; e.g., widths and shifts of states, possible multiple interactions, and dispersion corrections due to the relatively sensitive variation of the refractive index near resonance.

CHAPTER III

SCATTERING FROM FREE ELECTRONS IN A PLASMA

Over a wide range of incident frequencies away from resonance, single free electrons have larger light scattering cross sections than many molecules by several orders of magnitude. This fact is evident from Table 3.1. Thus in a system which contains a significant number of free electrons, these electrons may be the dominant scatterers. Even if the free electron scattering does not dominate it will often be distinguishable from scattering by atoms because of pronounced differences in the frequency distributions of light scattered from the two types of particles.

Much of the current interest in scattering from free electrons arises from theoretical indications that such scattering in a plasma ought to reveal valuable, difficult-to-obtain information about the plasma, in particular about the electron density and velocity distribution. Although the scattering experiments are not easy, this promise has been sufficient to inspire numerous sustained experimental efforts. Judging from recently published reports,[45] a significant number of these efforts have attained reasonable success, and light scattering appears to be becoming a well established diagnostic tool.

In this chapter are discussed the steps necessary to obtain from the general scattering cross section given by Eq. (1.59) the expression

TABLE 3.1

RAYLEIGH SCATTERING CROSS SECTIONS AT 6943 Å

(The cross sections are equivalent to σ_{zz}^{Ray} as defined by Eq. (4.29). They are also equal to σ_{zz}^{CD}, as defined in Eq. (4.17), to within a few percent. The particles are in ground states unless otherwise indicated.)

Particle	σ_{zz}^{Ray} in cm^2/steradian	
Free electron	$.79 \times 10^{-25}$	(a)
H atom	2.4×10^{-28}	(b)
H atom in 2S metastable state	6.12×10^{-23}	(c)
A	$.843 \times 10^{-28}$	(d)
Xe	5.71×10^{-28}	(d)
N_2	1.04×10^{-28}	(d)
Cs atom	$.89 \times 10^{-25}$	(e)

(a) Heitler[52]

(b) Mittleman and Wolf[74]

(c) Wolfgang Zernik[75]

(d) George *et al.*[61]

(e) Section 4.4, Fig. 4.3, this dissertation.

for the free electron light scattering cross section which serves as a starting point for many of the published (quantum and classical) theoretical analyses of free electron scattering.

The cross section given by Eq. (1.59) should apply to a plasma system at least as long as

a) the incident frequency is well above the plasma frequency and not too near resonance with atomic or molecular levels in the system, and

b) the incident beam is not too intense or too finely focussed.*

In order to obtain from this equation the desired expression for the free electron cross section, first it is necessary to neglect the second-order contribution to the free electron scattering in Eq. (1.59), that is, to neglect

$$\sum_{j\ell}\sum_{\mathcal{B}''}\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{r}_\ell}\,p_{\ell 2}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{r}_j}\,p_{j1}|\mathcal{B}\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}} - \frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{r}_j}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{r}_\ell}\,p_{\ell 2}|\mathcal{B}\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}}\right\} \tag{3.1}$$

This approximation is not difficult to justify in the ideal gas, for then using the arguments presented in Appendix C one may show directly that the terms in (3.1) for which $j\neq\ell$ vanish, whereas the terms for which $j=\ell$ are of order v_j/c times the first-order free electron contributions or smaller; that is, they are relativistic terms of the type which ought to be neglected in a nonrelativistic treatment.

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*These conditions are established more precisely in Chapter I and the references quoted therein.

Detailed theoretical analyses[38,39,40] which, however, neglect the resonance contributions of (3.1), suggest that the free electrons scatter light just as an ideal gas as long as the condition

$$\lambda_D \gg \frac{\lambda_1}{4\pi \sin \theta/2} \tag{3.2}$$

is satisfied. Here λ_D is the Debye length characteristic of the plasma, λ_1 is the incident wavelength and θ is the angle of scatter as defined in Fig. 4.2. It is apparent from Fig. 3.1 that the ideal gas approximation is acceptable except in relatively cold, dense plasmas and/or small angle scattering. One might argue that if the ideal gas approximation is acceptable for the first-order contribution to the scattering it is probably also acceptable for the second-order contribution, in which case the latter would introduce negligible corrections.

However, for the case of light scattering at very small angles and/or from dense plasmas, or the case of radar wave scattering from the ionosphere, inequality (3.2) is no longer satisfied and detailed theoretical analyses of the scattering (again considering only the direct scattering contributions) indicate that it will be markedly different from that predicted from the ideal gas approximation. The characteristics of the scattering in this region may be described qualitatively as follows:* First the central Doppler-broadened peak

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*This qualitative description is based on the quantitative results of Lamb.[38] We assume that electrons and ions are in Maxwellian velocity distributions at approximately equal temperatures.

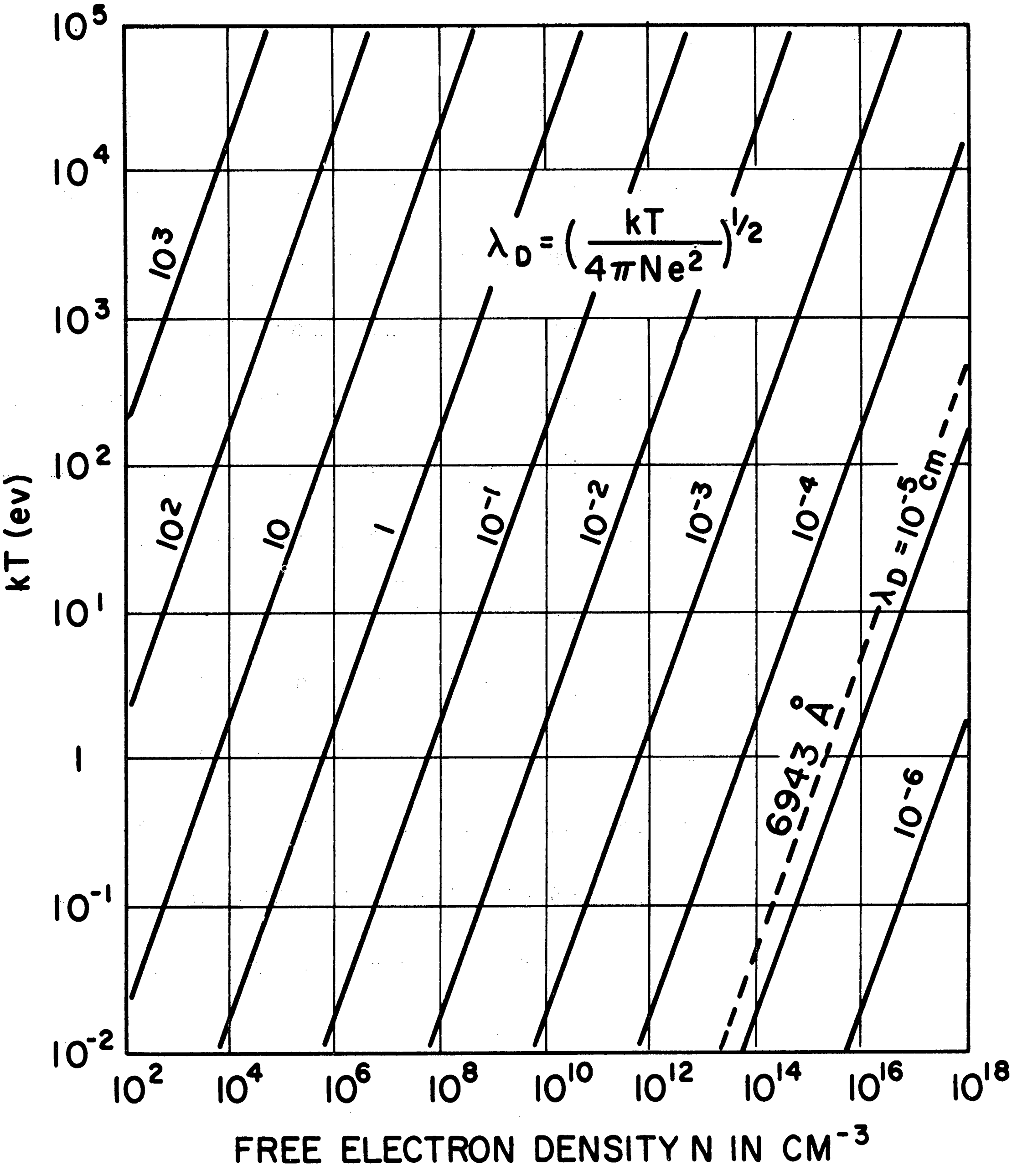

Fig. 3.1. Debye length versus plasma density and temperature for singly charged particles.

which is present in the ideal gas becomes much narrower, in fact approaching the width of the peak corresponding to Doppler broadening from the more slowly moving ions. Since in the ideal gas the Doppler broadening arises from energy exchanges necessary to conserve momentum between the scattering photon and the particle from which it scatters, narrowing of the central peak suggests that more than one particle is taking up the recoil momentum $\hbar\kappa$; in particular it appears that an ion is taking up most of the recoil momentum. This phenomenon bears an interesting analogy to the Mossbauer effect.

Second, satellite peaks appear distributed symmetrically about the main peak. These peaks can be associated with exchanges of energy between scattering photons and the collective modes of the plasma, in particular with those associated with the plasma frequency. This phenomenon bears some analogy to Brillouin scattering, although in a plasma the long range coulomb forces rather than short range intermolecular forces are supporting the collective modes.

These results arise from the first-order contribution to free electron scattering in Eq. (1.59). However, it is not completely clear that the second-order contribution to the free electron scattering is negligible, particularly in the case where the scattering differs markedly from that predicted by the ideal gas approximation. In fact, as particle-particle interactions become more significant, the trend is for the relative importance of the second-order terms to increase. This statement is based on the fact that in the extreme case in which the electrons are bound, the second-order term for light scattering (as opposed to x-ray scattering) is almost always comparable to or larger than the first order term.*

Dubois and Gilinski[40] have devoted some attention to the possible significance of the second-order terms, using Green's function techniques. Nevertheless, this issue does not seem to be completely resolved at the present time and further consideration of the second-order terms may be warranted, particularly under conditions where (3.2) fails.

Henceforth we will fall into step, assuming that the second-order contribution to the free electron scattering is negligible. Then more than a few angstroms away from resonance with discrete atomic or molecular transitions, the scattering from a plasma is described by Eq. (1.59). Using the methods of Chapter II this cross section may be put into the form

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\sigma^{c}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2) \qquad (3.3)$$

$$+\sigma^{I}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)$$

$$\sigma^{c}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\beta\beta'}P_\beta\, a^{*}_{\beta\beta}\, a_{\beta'\beta'} \qquad (3.4)$$

$$(x)\int d^3\rho\, d\tau\, e^{i(\underline{K}\cdot\underline{\rho}-\omega\tau)}\, G_{\beta\beta'}(\underline{\rho},\tau)$$

$$\sigma^{I}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2)=\frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\beta\beta'}P_\beta\,|a_{\beta'\beta}|^2 \qquad (3.5)$$

$$(x)\int d^3\rho\, d\tau\, e^{i[\underline{K}\cdot\underline{\rho}+(\omega_{\beta'\beta}-\omega)\tau]}\, G^{s}_{\beta}(\underline{\rho},\tau)$$

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*See Section 4.1 of Chapter IV.

where

$$G_{\beta\beta'}(\rho,\tau) = G^{s}_{\beta}(\rho,\tau)\delta_{\beta\beta'} + G^{p}_{\beta\beta'}(\rho,\tau) \qquad (3.6)$$

Equations (2.39) and (2.40) have been combined to give Eq. (3.4) whereas Eq. (3.5) is identical with Eq. (2.41). All of the free electron scattering is contained in the coherent scattering cross section.

It is apparent from Eq. (3.4) that the scattering from free electrons may interfere with the coherent scattering from atoms, ions and molecules. The interference depends on the Van Hove G-functions $G_{\beta\beta'}(\rho_-,\tau)$ which describe correlations between different types of particles. However, as noted previously the light scattering cross section for a single free electron is several orders of magnitude larger than the corresponding cross section for most atoms and simple molecules. This situation is illustrated in Table 3.1 with two interesting exceptions.

The fact that the free electron cross section is larger implies that the quantity $a_{\beta\beta}$ for a free electron will be larger, the ratio being equal to the square root of the ratio of single particle cross sections. Thus in many cases to a good approximation one need consider only the free electrons as scatterers. An extreme case is scattering from a fully ionized hydrogen plasma. For this case only the free electron terms contribute to Eq. (3.3). The scattering from the hydrogen nuclei is not included in Eq. (1.59); it was omitted in Chapter I along with other terms of similar magnitude which make up the center-of-mass correction.

Neglecting all scatterers except free electrons, and neglecting the second-order free electron contributions, the scattering cross section becomes

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi\omega_1}\left(\frac{e^2}{mc^2}\right)^2(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)^2$$
$$(\times)\int d^3\rho\, d\tau\, e^{i(\underline{k}\cdot\underline{\rho}-\omega\tau)}\, G_{ee}(\underline{\rho},\tau), \tag{3.7}$$

where the subscript e designates free electrons. In the Vineyard perscription classical limit* this result is identical to the cross section derived from classical electromagnetic theory and used as a starting point, for example, by Lamb,[38] and by Rosenbluth and Rostoker.[39]

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*See the discussion following Eq. (2.35) for a description of the Vineyard perscription.

CHAPTER IV

DEPENDENCE OF SCATTERING CROSS SECTIONS ON INTERNAL STATES

In Chapter II we have shown that the dependence of light scattering cross sections in gases on external and internal states may be treated separately away from resonance. In Section 4.1 the dependence on internal states is developed into a familiar form. In Section 4.2 the internal state angular dependence of the cross sections are determined and expressed in several convenient forms. In Section 4.3, relations between cross sections, oscillator strengths, and refractive indices are developed and examined. In Section 4.4, the Rayleigh scattering cross sections for ground state cesium atoms are calculated from oscillator strengths and used to illustrate some of the points raised in previous sections. Finally, in Section 4.5, the relationship between the charge symmetry of the scattering particles and the depolarization of the scattered radiation is investigated briefly.

4.1 DEVELOPMENT OF THE SCATTERING CROSS SECTION DEPENDENCE ON INTERNAL STATES

The dependence of the scattering cross sections developed in Chapter II on internal states is contained in the expressions $|a_{\beta'\beta}|^2$ and $a^*_{\beta\beta}\, a_{\beta'\beta'}$ which appear in these cross sections. The quantity $a_{\beta'\beta}$ is defined by Eq. (2.22), from which we obtain (4.1)

$$a_{\beta'\beta} = Z_\beta (\underline{\epsilon}_1 \cdot \underline{\epsilon}_2)\delta_{\beta'\beta} + \frac{1}{\hbar m}\sum_{\beta''}\left\{\frac{\langle\beta'|\Pi_2|\beta''\rangle\langle\beta''|\Pi_1|\beta\rangle}{\omega_1 - \omega_{\beta''\beta}} - \frac{\langle\beta'|\Pi_1|\beta''\rangle\langle\beta''|\Pi_2|\beta\rangle}{\omega_1 + \omega_{\beta''\beta'}}\right\}$$

In order to obtain Eq. (4.1), ω_2 in Eq. (2.23) has been evaluated at the center of the line corresponding to the transition $\beta \to \beta'$, for which

$$\omega_2 \cong \omega_1 - \omega_{\beta'\beta}$$

This approximation appears to be excellent for all cross sections of present concern at least away from resonance.

Both the first- and second-order terms in Eq. (4.1) contribute to coherent scattering. For nonresonance scattering of light, they are usually of approximately the same magnitude and opposite sign, such that they tend to cancel each other. This point is apparent from the following argument: The coherent direct cross section is usually the dominant contribution to the Rayleigh cross section in a gaseous scattering system. If this cross section is calculated from only the first order terms in Eq. (2.61) in the ideal gas approximation, one obtains

$$\begin{aligned} \sigma^{CD}(\underline{\epsilon}_1 \omega_1 \underline{\Omega}_1 \to \underline{\epsilon}_2 \underline{\Omega}_2) &= \left(\frac{e^2}{mc^2}\right)^2 (\underline{\epsilon}_1 \cdot \underline{\epsilon}_2)^2 Z^2 \qquad (4.2) \\ &\cong .79 \times 10^{-25} (\underline{\epsilon}_1 \cdot \underline{\epsilon}_2) Z^2 \ cm^2 \end{aligned}$$

However, this cross section is larger than the observed Rayleigh cross sections of most atoms and simple molecules away from resonance by at least two orders of magnitude. Therefore, at least when the observed cross section is much smaller than that given by Eq. (4.2) we are led to conclude that the second-order contribution is nearly equal to the first-order contribution in magnitude and opposite in sign so that the two contributions tend to cancel. Since this situation obtains for most atoms and molecules for Rayleigh scattering away from resonance,* it appears that the second-order term is almost always significant in light scattering cross sections. (Of course, only the second-order terms contribute to incoherent scattering.)

In fact, using the manipulations to be presented in this section one can show that in the limit $\omega_1 \rightarrow 0$ the first- and second-order terms exactly cancel. As ω_1 increases from zero, the coherent direct cross section also increases from zero with the well known ω_1^4 dependence until the resonance region is approached. This increase is associated with the slow increase of the second-order term with ω_1 from an initial ($\omega_1=0$) value equal to the negative of the first-order term.

Rather than consider separately the first- and second-order contributions to the coherent scattering cross section, it is possible and convenient to combine them through manipulations which have been presented by Dirac.[51] The combined form is also convenient for the incoherent scattering cross sections to which only the second-order term contributes. In this case the second-order term is merely expressed in another form. One may effect this combination in the following way: Consider the expression

$$\sum_{\beta''}\left\{\langle\beta'|\pi_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle-\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\pi_2|\beta\rangle\right\}=\langle\beta'|[\pi_2,\rho_1]|\beta\rangle \quad (4.3)$$

The right hand side is obtained upon summing over intermediate states.

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*See Table 3.1.

Noting that π_2 and ρ_1 are sums of canonically-conjugate momentum and position components, it is easily shown that

$$\langle\beta'|\,[\pi_2,\rho_1]\,|\beta\rangle = -i\hbar\, Z_\beta\, (\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\,\delta_{\beta'\beta} \tag{4.4}$$

From Eqs. (4.3) and (4.4), the first-order term in Eq. (4.1) may be written in the form

$$Z_\beta(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\delta_{\beta'\beta} = \frac{i}{\hbar}\sum_{\beta''}\left\{\langle\beta'|\pi_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle - \langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\pi_2|\beta\rangle\right\} \tag{4.5}$$

The second-order term may be put into a similar form by employing the relation

$$\pi_j = \frac{im}{\hbar}\left[H^N_\beta,\rho_j\right] \tag{4.6}$$

Here j designates a vector component. One may demonstrate directly that this relation is rigorous for the Hamiltonian

$$H^N_\beta = \sum_j^{Z_\beta} \frac{\pi_j^2}{2m} + V(\underline{\rho}_1,\cdots,\underline{\rho}_{Z_\beta}) \tag{4.7}$$

However, H^N_β as given by Eq. (1.15) contains additional terms of the form $1/2M \sum_{j\ell}^{Z_\beta\,\prime} \pi_j\cdot\pi_\ell$. The contribution of these terms to the commutator in Eq. (4.6) is included in the center-of-mass corrections which we have argued may be ignored to an excellent approximation. (See the comments following Eq. (1.36).) Furthermore, it is often necessary to add a spin Hamiltonian to (4.7) along with a term describing spin orbit interactions of the form $A(\rho_-)\underline{S}\cdot\underline{L}$. The former does not contribute to the commutator and the contribution of the latter term to the commutator may be shown to be negligible as far as light scattering is concerned.

Substituting from Eq. (4.6) for π_1 in the second-order term in Eq. (4.1), one obtains

$$\sum_{\beta''}\left\{\frac{\langle\beta'|\pi_2|\beta''\rangle\langle\beta''|\pi_1|\beta\rangle}{\omega_1-\omega_{\beta''\beta}}-\frac{\langle\beta'|\pi_1|\beta''\rangle\langle\beta''|\pi_2|\beta\rangle}{\omega_1+\omega_{\beta''\beta'}}\right\} \tag{4.8}$$

$$=im\sum_{\beta''}\left\{\frac{\omega_{\beta''\beta}}{\omega_1-\omega_{\beta''\beta}}\langle\beta'|\pi_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle+\frac{\omega_{\beta''\beta'}}{\omega_1+\omega_{\beta''\beta'}}\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\pi_2|\beta\rangle\right\}$$

Substituting this result and Eq. (4.5) into Eq. (4.1), one obtains

$$a_{\beta'\beta}=\frac{i\omega_1}{\hbar}\sum_{\beta''}\left\{\frac{\langle\beta'|\pi_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle}{\omega_1-\omega_{\beta''\beta}}-\frac{\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\pi_2|\beta\rangle}{\omega_1+\omega_{\beta''\beta'}}\right\}$$

It is convenient to employ Eq. (4.6) once more, substituting for π_2. This step yields

$$a_{\beta'\beta}=\frac{m\omega_1}{\hbar}\sum_{\beta''}\left\{\frac{\omega_{\beta''\beta'}}{\omega_1-\omega_{\beta''\beta}}\langle\beta'|\rho_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle+\frac{\omega_{\beta''\beta}}{\omega_1+\omega_{\beta''\beta'}}\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\rho_2|\beta\rangle\right\} \tag{4.9}$$

Note that

$$\sum_{\beta''}\left\{\langle\beta'|\rho_2|\beta''\rangle\langle\beta''|\rho_1|\beta\rangle-\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\rho_2|\beta\rangle\right\}=0 \tag{4.10}$$

Adding this null contribution to Eq. (4.9), one obtains finally

$$a_{\beta'\beta}=\frac{m}{\hbar}\omega_1(\omega_1-\omega_{\beta'\beta})\sum_{\beta''}\left\{\frac{\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\rho_2|\beta\rangle}{\omega_1-\omega_{\beta''\beta}}-\frac{\langle\beta'|\rho_1|\beta''\rangle\langle\beta''|\rho_2|\beta\rangle}{\omega_1+\omega_{\beta''\beta'}}\right\} \tag{4.11}$$

It is convenient to introduce the quantity

$$(C_{12})_{\beta\to\beta'}\equiv\frac{1}{\hbar}\sum_{\beta''}\left\{\frac{\langle\beta|D_1|\beta''\rangle\langle\beta''|D_2|\beta'\rangle}{\omega_{\beta''\beta}-\omega_1}+\frac{\langle\beta|D_2|\beta''\rangle\langle\beta''|D_1|\beta'\rangle}{\omega_{\beta''\beta'}+\omega_1}\right\} \tag{4.12}$$

where $\underline{D}$ is the dipole moment operator defined by

$$\underline{D} = e\underline{p} \tag{4.13}$$

Comparing Eqs. (4.13) and (4.12), it is evident that

$$(C_{12})_{\beta\to\beta'} = -\frac{e^2}{m\omega_1(\omega_1 - \omega_{\beta'\beta})}\, a^*_{\beta'\beta} \tag{4.14}$$

Note that $(C_{12})_{\beta\beta'}$ can be written

$$(C_{12})_{\beta\to\beta'} = \epsilon_{1j}\,\epsilon_{2\ell}\,(C_{j\ell})_{\beta\to\beta'} \tag{4.15}$$

where

$$(C_{j\ell})_{\beta\to\beta'} \equiv \frac{1}{\hbar}\sum_{\beta''}\left\{\frac{\langle\beta|D_j|\beta''\rangle\langle\beta''|D_\ell|\beta'\rangle}{\omega_{\beta''\beta} - \omega_1} + \frac{\langle\beta|D_\ell|\beta''\rangle\langle\beta''|D_j|\beta'\rangle}{\omega_{\beta''\beta'} + \omega_1}\right\} \tag{4.16}$$

Here j and ℓ designate vector components along the axis of a rectilinear coordinate system. The components $(C_{j\ell})_{\beta\beta'}$ represent the well known polarizability tensor or scattering tensor. This quantity is employed frequently in the literature to describe interactions between radiation and atoms or molecules.

In terms of $(C_{12})_{\beta\beta'}$, the scattering cross sections presented in Chapter II assume the forms

$$\sigma^{CD}(\underline{\epsilon}_1\omega_1\Omega_1 \to \underline{\epsilon}_2\Omega_2) = \sigma^{CD}_{12} \equiv \sum_{\beta} P_\beta\,(\sigma_{12})_{\beta\to\beta} \tag{4.17}$$

$$\sigma^{B\to B'}(\underline{\epsilon}_1\omega_1\Omega_1 \to \underline{\epsilon}_2\Omega_2) = \sigma^{B\to B'}_{12} \equiv \sum_{\beta}^{B} P_\beta \sum_{\beta'}^{B'}{}' (\sigma_{12})_{\beta\to\beta'} \tag{4.18}$$

$$\sigma^{I\,Ray}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\underline{\Omega}_2) = \sigma_{12}^{I\,Ray} \equiv \sum_{B}^{B} \sum_{\beta\beta'} P_\beta (\sigma_{12})_{\beta\rightarrow\beta'} \qquad (4.19)$$

where

$$(\sigma_{12})_{\beta\rightarrow\beta'} \equiv \frac{\omega_1(\omega_1-\omega_{\beta'\beta})^3}{c^4} \left| (C_{12})_{\beta\rightarrow\beta'} \right|^2 \qquad (4.20)$$

Finally,

$$\sigma^{CN}(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\underline{\Omega}_2) = \frac{\omega_1^4}{c^4} \sum_{\beta\beta'} P_\beta \, (C_{12})^*_{\beta\rightarrow\beta'} (C_{12})_{\beta\rightarrow\beta'} \qquad (4.21)$$

$$(x) \int d^3\rho \, e^{i\underline{K}_0\cdot\underline{\rho}} \, g_{\beta\beta'}(\underline{\rho})$$

The shorter notation introduced in Eqs. (4.17), (4.18) and (4.19) facilitates subsequent manipulations.

Similar expressions are obtained for the final frequency dependent cross sections discussed in Sections 2.1, 2.2, and 2.3 of Chapter II. These cross sections are in agreement with the results of Placzek* and Dirac,[51] among others.

4.2. ANGULAR DEPENDENCE OF THE CROSS SECTIONS ON INTERNAL STATES

In this section the internal state angular dependence of the scattering cross sections developed in Chapter II are derived and examined. The results are compared with those of the classical theory as presented by Born,[23] and with the quantum results obtained previously by Placzek.[34] The classical and quantum results agree (as far as the angular dependences are concerned). The present derivation is offered because it appears to be considerably simpler and shorter than previous derivations.

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*Ref. 34, Chapter 5, Eq. (5.4).

From Eqs. (4.17) through (4.21) it is evident that $|(C_{12})_{\beta\rightarrow\beta'}|^2$ and $(C_{12})^*_{\beta\beta}\ (C_{12})_{\beta'\beta'}$ contain the internal state angular dependences of the cross sections. In order to analyze these dependences, it is convenient to introduce a rectilinear coordinate system defined such that $\underline{\epsilon}_1$ is parallel to the z-axis and $\underline{\epsilon}_2$ is in the xz-plane. Then

$$D_1 = D_z \tag{4.22}$$

and

$$D_2 = D_z \cos\psi + D_x \sin\psi \tag{4.23}$$

Here ψ is the angle between $\underline{\epsilon}_1$ and $\underline{\epsilon}_2$. Substituting these expressions into Eq. (4.12), one obtains

$$(C_{12})_{\beta\rightarrow\beta'} = \frac{1}{\hbar}\sum_{\beta''}\left\{\frac{\langle\beta|D_z|\beta''\rangle\langle\beta''|D_z\cos\psi + D_x\sin\psi|\beta'\rangle}{\omega_{\beta''\beta} - \omega_1}\right. \tag{4.24}$$

$$\left. + \frac{\langle\beta|D_z\cos\psi + D_x\sin\psi|\beta''\rangle\langle\beta''|D_z|\beta'\rangle}{\omega_{\beta''\beta'} + \omega_1}\right\}$$

This equation may be simplified using certain properties of the single particle internal state functions $|\beta\rangle$. These properties result from the fact that the zero-order Hamiltonian for the scattering system, as given by Eq. (1.18), commutes with the total internal angular momentum operator $\hat{J}$ for any particular particle. It follows that the total internal angular momentum of each particle is conserved in direction and magnitude in the zero-order approximation, and that the state functions for any particular particle may be chosen to be eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$.* We denote the state functions so chosen by $|\tau JM\rangle$; these functions satisfy

$$\begin{aligned}\mathcal{H}|\tau JM\rangle &= E_{\tau J}|\tau JM\rangle\\ \hat{J}^2|\tau JM\rangle &= J(J+1)|\tau JM\rangle\\ \hat{J}_z|\tau JM\rangle &= M|\tau JM\rangle\end{aligned}$$

Here $\mathcal{H}$ represents the internal Hamiltonian for a single particle. For a demonstration of the important result that $E_{\tau J}$ is independent of the magnetic quantum number see Ref. 55, Section 2.7.

Well known selection rules apply to matrix elements of D_z and D_x between state functions of this type. For example, from Ref. 76, Chapter 10, Section 8

$$\begin{aligned}\langle\tau'J'M'|D_z|\tau JM\rangle &= 0\,, \quad M'\neq M\\ \langle\tau'J'M'|D_x|\tau JM\rangle &= 0\,, \quad M'\neq M\pm 1\end{aligned} \tag{4.25}$$

Introducing the eigenfunctions $|\tau JM\rangle$ into Eq. (4.24) and employing these selection rules, one may sum over M" directly to obtain

$$(C_{12})_{\tau JM\to\tau'J'M'} = \frac{1}{\hbar}\sum_{\tau''J''}\left\{\frac{\langle\tau JM|D_z|\tau''J''M\rangle\langle\tau''J''M|D_z\cos\psi + D_x\sin\psi|\tau'J'M'\rangle}{\omega_{\tau''J'',\tau J}-\omega_1}\right.$$
$$\left. + \frac{\langle\tau JM|D_z\cos\psi + D_x\sin\psi|\tau''J''M'\rangle\langle\tau''J''M'|D_z|\tau'J'M'\rangle}{\omega_{\tau''J'',\tau'J'}+\omega_1}\right\}$$

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*Note that if multipole interactions between particles and electric fields are included in the zero-order Hamiltonian or force the choice of state functions $|\beta\rangle$ which are not eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$, then these conclusions and those which follow are not valid in general.

Writing out the absolute square $|(C_{12})_{\tau JM\to\tau'J'M'}|^2$, it follows immediately from Eqs. (4.25) that the coefficients of sin ψ vanish if M'=M and the coefficients of cos ψ vanish if M'≠M. Therefore cross products between cos ψ and sin ψ terms vanish and the absolute square breaks up into two terms as follows:

$$|(C_{12})_{\tau JM\to\tau'J'M'}|^2 = \cos^2\psi\,|(C_{zz})_{\tau JM\to\tau'J'M'}|^2 + \sin^2\psi\,|(C_{zx})_{\tau JM\to\tau'J'M'}|^2$$

It follows from Eq. (4.20) that

$$(\sigma_{12})_{\tau JM\to\tau'J'M'} = \cos^2\psi\,(\sigma_{zz})_{\tau JM\to\tau'J'M'} + \sin^2\psi\,(\sigma_{zx})_{\tau JM\to\tau'J'M'} \tag{4.26}$$

Only the first term contributes if M=M'; only the second, if M≠M'.

The scattering in a direction perpendicular to both $\underline{\epsilon}_1$ and $\underline{\Omega}_1$ is conventionally referred to as transverse scattering. We define the ratio of the transverse scattering intensity with polarization perpendicular to $\underline{\epsilon}_1$ to that with polarization parallel to $\underline{\epsilon}_1$ to be the transverse depolarization ρ.* In a gas not near a critical point employing the static approximation and neglecting coherent interference scattering (see Section 2.4), the ratio of intensities is equal to the ratio of appropriate cross sections defined in Eqs. (4.17) through (4.19). Thus, for example, the line corresponding to a transition

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*Note that this depolarization is defined for linearly polarized incident light. Frequently in the literature the normal depolarization for unpolarized incident light is introduced.

from level B to level B' is given by

$$\rho_{B\to B'} = \frac{\sigma_{ZX}^{B\to B'}}{\sigma_{ZZ}^{B\to B'}} \tag{4.27}$$

The transverse depolarizations for lines corresponding to incoherent Rayleigh and coherent scattering are defined similarly. It should be noted that if several of the cross sections contribute to a line, the depolarization is given by the ratio of sums of these cross sections and is not equal to the sum of the depolarizations of the separate contributions in general.

Now we consider the implications of these results concerning the coherent scattering cross sections. By definition, for coherent scattering $\tau=\tau'$, $J=J'$, and $M=M'$. From Eq. (4.17) and the discussion following Eq. (4.26), σ_{ZX}^{CD} vanishes since $M=M'$. Thus from Eqs. (4.17) and (4.26), one obtains for the coherent direct cross section:

$$\sigma_{12}^{CD} = \cos^2\psi \sum_{\tau JM} P_{\tau JM} (\sigma_{ZZ})_{\tau JM\to\tau JM} \tag{4.28}$$

A similar expression can be developed for the coherent interference cross section as given by Eq. (4.21). Also one may apply these results to the final frequency dependent coherent cross sections of Chapter II. The <u>normal depolarization vanishes</u> for all coherent cross sections and the internal state angular dependence is contained in the factor $\cos^2\psi$.

Next we consider Rayleigh scattering. The Rayleigh scattering cross section is given by the sum of coherent direct, coherent interference, and incoherent Rayleigh cross sections. In Section 2.4 of

Chapter II it is shown that the contribution of the coherent interference scattering from most gaseous systems is extremely small. This contribution will be neglected in the discussion of Rayleigh scattering in this and the following sections, allowing the introduction of relatively simple notation. However, where significant, the coherent interference scattering may be included in a development of this type in a straightforward manner.

Adding the coherent direct and incoherent Rayleigh cross sections as given by Eqs. (4.17) and (4.19), one obtains

$$\sigma_{12}^{Ray} = \sum_{B} \sum_{\substack{\tau J M \\ \tau' J' M'}}^{B} P_{\tau J M} \left(\sigma_{12}\right)_{\tau J M \rightarrow \tau' J' M'} \tag{4.29}$$

Substituting for $(\sigma_{12})_{\tau J M \rightarrow \tau' J' M'}$ from Eq. (4.26), it follows that

$$\sigma_{12}^{Ray} = \cos^2\psi\, \sigma_{zz}^{Ray} + \sin^2\psi\, \sigma_{zx}^{Ray} \tag{4.30}$$

The normal depolarization for Rayleigh scattering is

$$\rho_0 = \frac{\sigma_{zx}^{Ray}}{\sigma_{zz}^{Ray}} \tag{4.31}$$

Note that ρ_0 must vanish for Rayleigh scattering involving initial and final states of vanishing total angular momentum. This conclusion follows since if J=J'=0 for each term in the sum in Eq. (4.30), then necessarily M=M'=0 and as a result each contribution to σ_{zx}^{Ray} must vanish. Thus depolarization should vanish for Rayleigh scattering from ground state argon or neon atoms, for which J=0 (but not completely in scattering from Xenon or Helium 3 atoms because of their nuclear spin—see Section 4.4).

For Rayleigh scattering, one obtains from Eqs. (4.30) and (4.31)

$$\sigma_{12}^{Ray} = \sigma_{zz}^{Ray}\left(\cos^2\psi + \rho_0 \sin^2\psi\right) \tag{4.32}$$

or

$$\sigma_{12}^{Ray} = \sigma_{zz}^{Ray}\left[(1-\rho_0)\cos^2\psi + \rho_0\right] \tag{4.33}$$

This cross section is completely determined by the quantities σ_{zz}^{Ray} and ρ_0, both of which can be measured in a transverse scattering experiment. In the next section we shall show that under certain conditions both of these quantities can also be calculated from oscillator strengths and furthermore σ_{zz}^{Ray} may be related to a corresponding refractive index.

The classical theory of light scattering from molecules as developed by Born leads to a relationship between the Rayleigh scattering cross section and refractive index given by*

$$\sigma_{12}^{Ray} = \frac{\omega_1^4}{c^4}\left\{\left[\left(\frac{n^2-1}{4\pi\mathcal{N}}\right)^2 + \frac{\Omega}{3}\right]\cos^2\psi + \Omega\right\} \tag{4.34}$$

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*Ref. 23, Chapter VII, Section 81 from Eq. (5.2).

Here n is the index of refraction measured at a particle density $\mathcal{N}$ This equation is valid for incident frequencies far removed from resonance compared to widths of the corresponding states.* Taking the ratio of the cross sections evaluated for $\psi = \pi/2$ and $\psi = 0$, one obtains for the normal depolarization (for linearly polarized incident radiation)

$$\rho_o = \frac{\Omega}{\left(\frac{n^2-1}{4\pi\mathcal{N}}\right)^2 + \frac{4}{3}\Omega} \tag{4.35}$$

Substituting from this equation for Ω in Eq. (4.34) one obtains

$$\sigma_{12}^{Ray} = \frac{\omega_1^4}{c^4}\left(\frac{n^2-1}{4\pi\mathcal{N}}\right)^2\left(\frac{3}{3-4\rho_c}\right)\left[(1-\rho_o)\cos^2\psi + \rho_o\right] \tag{4.36}$$

Comparing Eqs. (4.33) and (4.36) it is apparent that the <u>angular</u> dependence of the quantum and classical Rayleigh cross sections are identical.

The scattering cross section for any particular Raman line may also be put into the form of Eq. (4.33). For example, for the line corresponding to the transition B→B' we obtain

$$\sigma_{12}^{B\rightarrow B'} = \sigma_{zz}^{B\rightarrow B'}\left[(1-\rho_{B\rightarrow B'})\cos^2\psi + \rho_{B\rightarrow B'}\right] \tag{4.37}$$

Here $\sigma_{zz}^{B\rightarrow B'}$ is defined by Eq. (4.18) and $\rho_{B\rightarrow B'}$, by Eq. (4.27). Again the angular dependence agrees with that obtained by Born from classical arguments.

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*See footnote on previous page and also Ref. 23, Chapter VII, Section 73.

It is helpful upon occasion to express Eqs. (4.33) and (4.37) in terms of scattering angles rather than the angle between polarizations. A number of different schemes may be used to define scattering angles. One scheme which is useful when the incident radiation is linearly polarized is illustrated in Fig. 4.1. In terms of the angles ξ and ϕ, this scheme yields

$$\cos\psi = \cos\xi\sin\phi \tag{4.38}$$

Of particular interest for comparison with previous quantum results of Placzek[34] is the cross section summed over final polarizations. One may sum over any two orthogonal final polarizations, but the most convenient are those for which $\xi=0$ and $\xi = \pi/2$. Substituting Eq. (4.38) into Eq. (4.33) or Eq. (4.37) and performing this sum, one obtains

$$\sigma_{12} = \sigma_{zz}\left[(1+\rho)-(1-\rho)\cos^2\phi\right] \tag{4.39}$$

This result agrees with that obtained by Placzek from a different formulation of the cross section. Placzek's formulation is well suited for the derivation of symmetry selection rules (see Section 4.5) but does not yield directly the final polarization dependent scattering cross sections such as in Eq. (4.33).

For cases in which the incident beam is not totally polarized, perhaps the most useful scheme for expressing scattering angles is that illustrated in Fig. 4.2. Note that

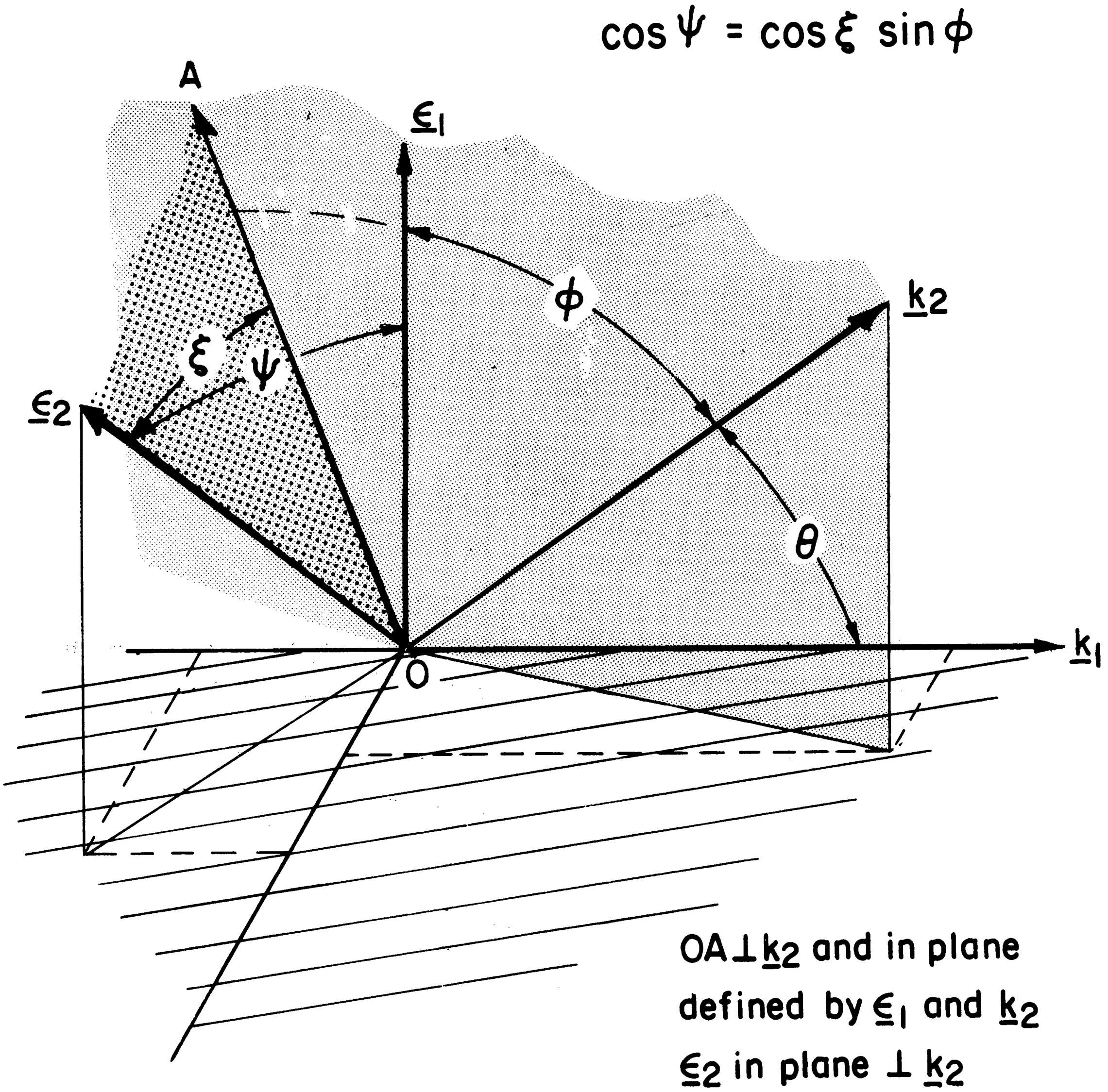

Fig. 4.1. Relationship between polarization angle ψ and scattering angles φ and ξ.

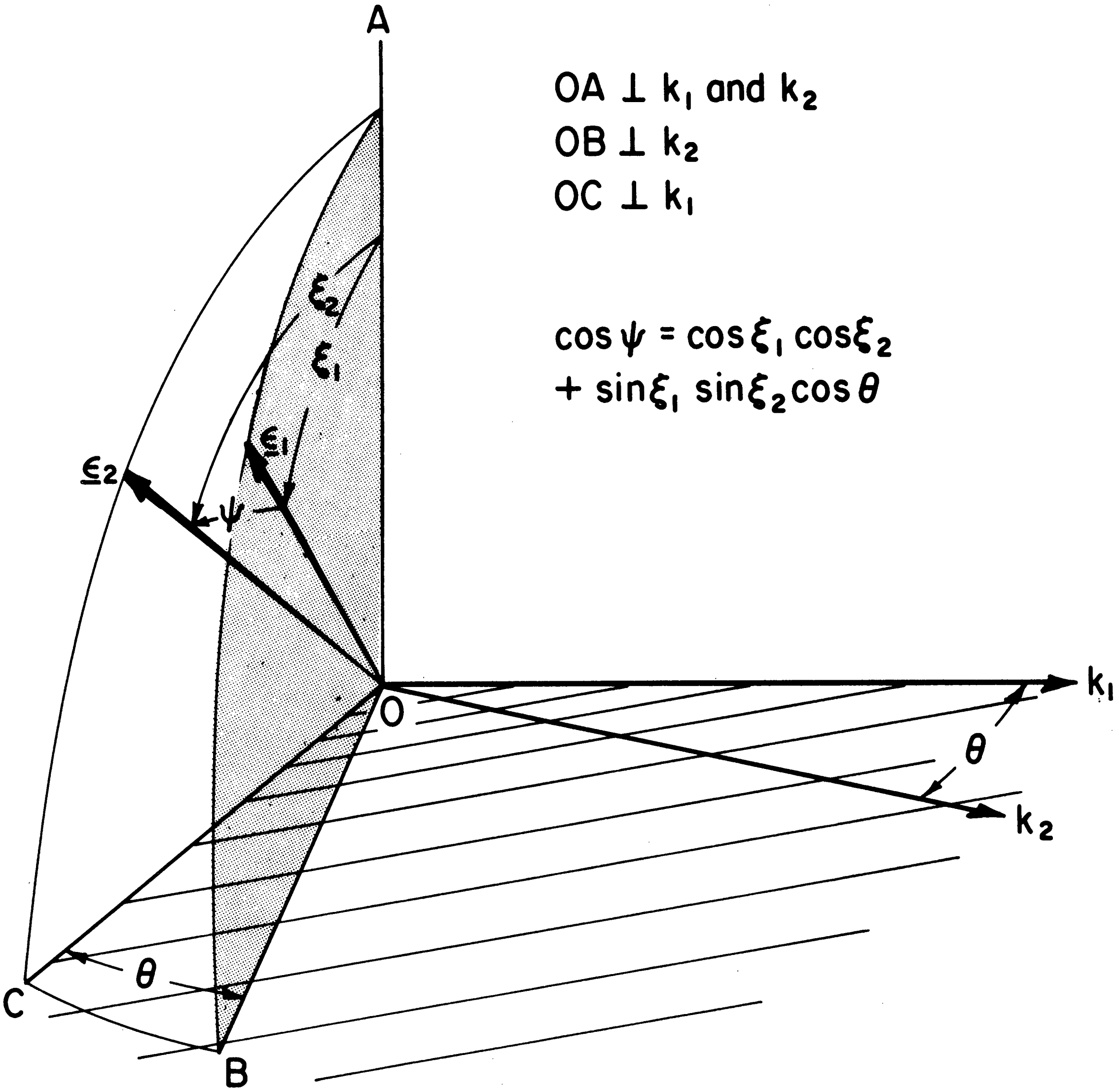

Fig. 4.2. Relationship between polarization angle ψ and scattering angles Θ, ξ_1 and ξ_2.

$$\cos\psi = \cos\xi_1 \cos\xi_2 + \sin\xi_1 \sin\xi_2 \cos\Theta \tag{4.40}$$

This result may be substituted into Eqs. (4.28), (4.33), and (4.37) in order to obtain the angular dependences of the cross sections in terms of the scattering angles ξ_1, ξ_2, and Θ. A number of special cases are of interest:

Case 1: $\xi_1=0$. Then

$$\sigma_{12} = \sigma_{zz}\left[(1-\rho)\cos^2\xi_2 + \rho\right] \tag{4.41}$$

If the polarization of the scattered beam is not analyzed, then one must sum over the unobserved polarizations. These may be chosen such that $\xi_2=0$ and $\pi/2$, yielding

$$\sigma_{12} = \sigma_{zz}(1+\rho) \tag{4.42}$$

Case 2: $\xi_1=\pi/2$. Then

$$\sigma_{12} = \sigma_{zz}\left[(1-\rho)\sin^2\xi_2\cos^2\Theta + \rho\right] \tag{4.43}$$

If the polarization of the scattered beam is not observed

$$\sigma_{12} = \sigma_{zz}\left[(1-\rho)\cos^2\Theta + 2\rho\right] \tag{4.44}$$

Case 3: Monochromatic incident beam partially polarized. If the polarization of the incident beam is resolved into x and y components, one obtains from Eq. (2.51) for the scattering of a monochromatic beam from a volume V_S

$$I_S(R\,|\,\underline{e}_2\underline{\Omega}_2) = \frac{V_S N_0}{R^2}\Big\{ I(\underline{e}_x\omega_1\underline{e}_y)\,\sigma_{x2} + I(e_z\omega_1 e_y)\,\sigma_{z2}\Big\} \tag{4.45}$$

Defining

$$I(\omega_1\underline{e}_y) = I(\underline{e}_x\omega_1\underline{e}_y) + I(\underline{e}_z\omega_1\underline{e}_y) \tag{4.46}$$

and

$$\Lambda = I(\underline{e}_x\omega_1\underline{e}_y)/I(\omega_1\underline{e}_y) \tag{4.47}$$

then

$$I_S(R\,|\,\underline{e}_2\underline{\Omega}_2) = \frac{V_S N_0}{R^2} I(\omega_1\underline{e}_y)\Big[\Lambda\sigma_{x2} + (1-\Lambda)\sigma_{z2}\Big]$$

or

$$I_S(R\,|\,\underline{e}_2\underline{\Omega}_2) = \frac{V_S N_0}{R^2} I(\omega_1\underline{e}_y)\,\sigma_{z2}\Big\{\Lambda\big[(1-\rho)\sin^2\xi_2\cos^2\theta + \rho\big] + (1-\Lambda)\big[(1-\rho)\cos^2\xi_2 + \rho\big]\Big\} \tag{4.48}$$

Other special cases may be developed in a similar fashion.

4.3. RELATIONSHIPS BETWEEN SCATTERING CROSS SECTIONS, OSCILLATOR STRENGTHS, AND REFRACTIVE INDICES

In this section, the scattering cross section is expressed in a convenient form using the Wigner-Eckart theorem. Employing this expression, the relationships between Rayleigh and Raman cross sections and oscillator strengths are examined. It is shown that the Rayleigh scattering cross section and the corresponding depolarization can be calculated directly from appropriate oscillator strengths for particles in initial states degenerate only in the magnetic quantum number M. Likewise it is shown that Raman scattering cross sections and the corresponding depolarization can be calculated directly from oscillator strengths for ω_1 sufficiently near resonance with an intermediate level which is degenerate only in the magnetic quantum number. Finally, breaking up the scattering cross section into two parts which correspond, respectively, to isotropic and anisotropic components of the scattering tensor, a relationship between the Rayleigh scattering cross section and a quantum expression for the corresponding refractive index is developed. This relationship is compared to the classical relationship between these two quantities and it is shown that there is a significant difference between the quantum and classical results except in the case of scattering particles with vanishing angular momentum.

From Eq. (4.29), under the condition that all initial and final states of nonvanishing total angular momentum are degenerate in the magnetic quantum number M, the Rayleigh and Raman cross sections of interest involve

$$(\sigma_{i\gamma})_{\tau J \to \tau' J'} \equiv \frac{1}{2J+1} \sum_{M=-J}^{J} \sum_{M'=-J'}^{J'} (\sigma_{i\gamma})_{\tau J M \to \tau' J' M'} \qquad (4.49)$$

From Eqs. (4.49) and (4.20) and (4.16)

$$(\sigma_{i\gamma})_{\tau J\to\tau' J'} = \frac{\omega_1(\omega_1-\omega_{\tau'J',\tau J})^3}{\hbar^2 c^4 (2J+1)} \sum_{MM'} \left| \sum_{\tau''J''M''} \left\{ \frac{\langle \tau JM | D_i | \tau''J''M''\rangle \langle \tau''J''M'' | D_\gamma | \tau JM\rangle}{\omega_{\tau''J'',\tau J} - \omega_1} \right.\right.$$
$$\left.\left. + \frac{\langle \tau JM | D_\gamma | \tau''J''M''\rangle \langle \tau''J''M'' | D_i | \tau JM\rangle}{\omega_{\tau''J'',\tau J} + \omega_1} \right\} \right|^2 \qquad (4.50)$$

Because of the different ways in which the sums over M and M' enter the expressions for the oscillator strengths and refractive indices, it is convenient to express the dependence of the matrix elements involved in Eq. (4.50) on M explicitly. Such expressions arise from the general properties of angular momentum as developed, for example, by Condon and Shortley.[76] We utilize a concise statement of these properties in the form of the Wigner-Eckart theorem,* which allows one to write

$$\langle \tau JM | D_\mu | \tau' J' M'\rangle = (-1)^{J-M} \langle \tau J \| D \| \tau' J'\rangle \begin{pmatrix} J & 1 & J'' \\ -M & \mu & M'' \end{pmatrix} \qquad (4.51)$$

The quantities D_μ are the irreducible tensor components of the dipole moment operator $\underline{D}$, defined by

$$\begin{aligned} D_0 &= D_z \\ D_1 &= -\frac{\sqrt{2}}{2}(D_x + iD_y) \\ D_{-1} &= \frac{\sqrt{2}}{2}(D_x - iD_y) \end{aligned} \qquad (4.52)$$

such that

$$\begin{aligned} D_x &= -\frac{\sqrt{2}}{2}(D_1 - D_{-1}) \\ D_y &= \frac{i\sqrt{2}}{2}(D_1 + D_{-1}) \end{aligned} \qquad (4.53)$$

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*This theorem and related subjects are discussed in detail by Messiah.[54] We use the notation of this reference.

The reduced matrix elements $\langle \tau J \| D \| \tau' J' \rangle$ are independent of M and M'. The Wigner 3-J symbols $\begin{pmatrix} J_1 J_2 J_3 \\ M_1 M_2 M_3 \end{pmatrix}$ contain the M-dependence including the selection rules on M introduced previously as well as selection rules on J. The relevant properties of these symbols are well known,[54] and they have been extensively tabulated[88] for given values of J and M.

Applying the Wigner-Eckart theorem to Eq. (4.50) one obtains

$$(\sigma_{zz})_{\tau J \to \tau' J'} = \frac{\omega_1 (\omega_1 - \omega_{\tau' J', \tau J})^3}{\hbar^2 c^4 (2J+1)} \sum_{M=-J}^{J} \Bigg| \sum_{\tau'' J''} \frac{\omega_{\tau'' J'', \tau J} + \omega_{\tau'' J'', \tau' J'}}{(\omega_{\tau'' J'', \tau J} - \omega_1)(\omega_{\tau'' J'', \tau J} + \omega_1)} \tag{4.54}$$

$$(\times) \langle \tau J \| D \| \tau'' J'' \rangle \langle \tau' J' \| D \| \tau'' J'' \rangle^* \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ -M & 0 & M \end{pmatrix} \Bigg|^2$$

and

$$(\sigma_{zx})_{\tau J \to \tau' J'} = \frac{\omega_1 (\omega_1 - \omega_{\tau' J', \tau J})^3}{2\hbar^2 c^4 (2J+1)} \sum_{M=-J}^{J} \sum_{M'=-J'}^{J'} \Bigg| \sum_{\tau'' J''} \langle \tau J \| D \| \tau'' J'' \rangle \langle \tau' J' \| D \| \tau'' J'' \rangle^* \tag{4.55}$$

$$(\times) \left\{ \frac{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix} \left[\begin{pmatrix} J' & 1 & J'' \\ -M' & 1 & M \end{pmatrix} - \begin{pmatrix} J' & 1 & J'' \\ M' & -1 & M \end{pmatrix} \right]}{\omega_{\tau'' J'', \tau J} - \omega_1} + \frac{\left[\begin{pmatrix} J & 1 & J'' \\ -M & 1 & M' \end{pmatrix} - \begin{pmatrix} J & 1 & J'' \\ -M & -1 & M' \end{pmatrix} \right] \begin{pmatrix} J' & 1 & J'' \\ -M' & 0 & M' \end{pmatrix}}{\omega_{\tau'' J'', \tau' J'} + \omega_1} \right\} \Bigg|^2$$

Consider the Rayleigh scattering cross section for particles whose initial states are degenerate only in M. Then from Eq. (4.54), σ_{zz}^{Ray} is given by

$$(\sigma_{zz})_{\tau J \to \tau J} = \frac{\omega_1^4}{\hbar^2 c^4} \frac{4}{2J+1} \sum_{M} \Bigg| \sum_{\tau'' J''} \frac{\omega_{\tau'' J'', \tau J}}{\omega^2_{\tau'' J'', \tau J} - \omega_1^2} \left| \langle \tau J \| D \| \tau'' J'' \rangle \right|^2 \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \Bigg| \tag{4.56}$$

On the other hand, emission oscillator strengths for a line corresponding to a transition from a level $\tau'' J''$ to the level τJ are defined by[76]

$$f_{\tau''J''\rightarrow\tau J} = \frac{2m}{3e^2\hbar}\,\frac{\omega_{\tau''J'',\tau J}}{2J+1}\sum_{M}\sum_{M''}\left|\langle\tau J M|D|\tau''J''M''\rangle\right|^2 \qquad (4.57)$$

Employing the Wigner-Eckart theorem, this equation becomes

$$f_{\tau''J'',\tau J} = \frac{2m}{3e^2\hbar}\,\frac{\omega_{\tau''J'',\tau J}}{2J+1}\left|\langle\tau J\|D\|\tau''J''\rangle\right|^2 \qquad (4.58)$$

The sums over M and M" have been performed using an orthogonality property of the 3-J symbols.

Substituting from Eq. (4.58) for the absolute square of reduced matrix elements in Eq. (4.54), one obtains

$$(\sigma_{zz})_{\tau J\rightarrow\tau J} = 9\omega_1^4\left(\frac{e^2}{mc^2}\right)^2(2J+1)\sum_{M}\left|\sum_{\tau''J''}\frac{f_{\tau''J''\rightarrow\tau J}}{\omega^2_{\tau''J'',\tau J}-\omega_1^2}\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}^2\right|^2 \qquad (4.59)$$

Employing the same procedure, from Eq. (4.55) one obtains

$$(\sigma_{zx})_{\tau J\rightarrow\tau J} = \frac{9}{8}\,\omega_1^4\left(\frac{e^2}{mc^2}\right)^2(2J+1)\sum_{M}\sum_{M'}\left|\sum_{\tau''J''}\frac{f_{\tau''J''\rightarrow\tau J}}{\omega_{\tau''J'',\tau J}}\right. \qquad (4.60)$$

$$(\mathrm{X})\left\{\frac{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & 1 & M\end{pmatrix}}{\omega_{\tau''J'',\tau J}-\omega_1} - \frac{\begin{pmatrix} J & 1 & J'' \\ -M & -1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & 0 & M'\end{pmatrix}}{\omega_{\tau''J'',\tau J}+\omega_1}\right\}$$

From these results and Eq. (4.31) the normal depolarization may be calculated. It follows from Eq. (4.33) that if the relevant oscillator strengths are known, the Rayleigh scattering cross section may be calculated directly. An example of such a calculation for cesium atoms is presented in Section 4.4.

Now let us consider the relationship between Raman scattering cross sections and oscillator strengths. The following remarks apply also to Rayleigh scattering cross sections for particles whose initial states are degenerate in τ or J. These cross sections involve $(\sigma_{ij})_{\tau J\to\tau' J'}$ for $\tau' J' \neq \tau J$, as given by Eq. (4.50). From Eq. (4.58) it is apparent that the oscillator strengths $f_{\tau'' J''\to\tau J}$ yield the absolute squares of the reduced matrix elements, but reveal no information about their phases. Knowledge of the latter quantities is necessary in order to combine properly the contributions from various intermediate states within the absolute square in Eq. (4.50). Therefore, in general the oscillator strengths alone do not suffice for calculation of Raman cross sections. However, it often happens that sufficiently near resonance only one term in the sum over $\tau'' J''$, say $\tau_1 J_1$, is significant and for example, Eq. (4.50) may yield to a good approximation

$$(\sigma_{zz})_{\tau J\to\tau' J'} = \frac{\omega_1(\omega_1-\omega_{\tau' J',\tau J})^3}{\hbar^2 c^4 (2J+1)}\left(\frac{1}{\omega_{\tau_1 J_1,\tau J}-\omega_1}\right)^2 \tag{4.61}$$

$$(\times)\ \left|\langle \tau J\|D\|\tau_1 J_1\rangle\right|^2 \left|\langle \tau' J'\|D\|\tau_1 J_1\rangle\right|^2 \sum_M \begin{pmatrix} J & 1 & J_1\\ -M & 0 & M\end{pmatrix}^2 \begin{pmatrix} J' & 1 & J_1\\ -M & 0 & M\end{pmatrix}^2$$

or, in terms of oscillator strengths

$$(\sigma_{zz})_{\tau J\to\tau' J'} = \frac{9}{4}\,\frac{\omega_1(\omega_1-\omega_{\tau' J',\tau J})^3}{(\omega_{\tau_1 J_1,\tau J}-\omega_1)^2}\left(\frac{e^2}{mc^2}\right)^2 \tag{4.62}$$

$$(\times)\ \frac{2J'+1}{\omega_{\tau_1 J_1,\tau J}\,\omega_{\tau_1 J_1,\tau' J'}}\, f_{\tau_1 J_1\to\tau J}\, f_{\tau_1 J_1\to\tau' J'} \sum_M \begin{pmatrix} J & 1 & J_1\\ -M & 0 & M\end{pmatrix}^2 \begin{pmatrix} J' & 1 & J_1\\ -M & 0 & M\end{pmatrix}^2$$

Similar results are obtained for $(\sigma_{ZX})_{\tau J\to\tau' J'}$ sufficiently near resonance. In this situation the Raman cross section may be calculated directly from the relevant oscillator strengths. Of course very near resonance the widths and shifts of the intermediate states must be taken into account. For this case, following the notation of Appendix B, to a certain approximation the resonance denominator in Eq. (4.61) or (4.62) becomes

$$(\omega_{\tau_1 J_1, \tau J} - \omega_1)^2 + W^2_{\tau_1 J_1}$$

Now we wish to consider the relationship between Rayleigh scattering cross sections and the corresponding refractive indices. The classical relationship of this type is given by Eqs. (4.34) or Eq. (4.36). In order to demonstrate the quantum relationship it is convenient to develop the scattering cross section in a slightly different form. Starting from Eq. (4.12), we note that $(C_{12})_{\tau JM\to\tau' J' M'}$ may be written in the form

$$(C_{12})_{\tau JM\to\tau' J' M'} = \epsilon^1_\lambda \, \epsilon^2_\mu \, (C_{\lambda\mu})_{\tau JM\to\tau' J' M'} \tag{4.63}$$

Here the components $C_{\lambda\mu}$ of the scattering tensor are defined by

$$(C_{\lambda\mu})_{\tau JM\to\tau' J' M'} = \frac{1}{\hbar}\sum_{\tau'' J'' M''}\left\{\frac{\langle\tau J M|D_\lambda|\tau'' J'' M''\rangle\langle\tau'' J'' M''|D_\mu|\tau' J' M'\rangle}{\omega_{\tau'' J'', \tau J} - \omega_1}\right. \tag{4.64}$$

$$\left. + \frac{\langle\tau J M|D_\mu|\tau'' J'' M''\rangle\langle\tau'' J'' M''|D_\lambda|\tau J M\rangle}{\omega_{\tau'' J'', \tau' J'} + \omega_1}\right\}$$

The irreducible tensor components D_λ and D_μ are given by Eq. (4.52) and the components ϵ^1_λ and ϵ^2_μ of the vectors indicating initial and final polarization of the scattered photon are defined by

$$\begin{aligned} \epsilon^1_0 &= \epsilon_{1z} \\ \epsilon^1_1 &= -\frac{\sqrt{2}}{2}\left(\epsilon_{1x} - i\epsilon_{1y}\right) \\ \epsilon^1_{-1} &= \frac{\sqrt{2}}{2}\left(\epsilon_{1x} + i\epsilon_{1y}\right) \end{aligned} \tag{4.65}$$

and likewise for ϵ^2_μ. The quantities ϵ_{1x}, ϵ_{1y}, and ϵ_{1z} are components of $\underline{\epsilon_1}$ along the three orthogonal axes introduced to define components of $\underline{D}$ and $\hat{\underline{J}}$.

The scattering tensor may be expressed as the sum of an isotropic component $(C^0)_{\tau JM\to\tau'J'M'}$ and anisotropic components $(C^1_{\lambda\mu})_{\tau JM\to\tau'J'M'}$ as follows:

$$(C_{\lambda\mu})_{\tau JM\to\tau'J'M'} = \left[C^0\delta_{\lambda,-\mu}(-1)^\lambda + C^1_{\lambda\mu}\right]_{\tau JM\to\tau'J'M'} \tag{4.66}$$

$$(C^0)_{\tau JM\to\tau'J'M'} = \left[C_{00} - C_{1-1} - C_{-11}\right]_{\tau JM\to\tau'J'M'} \tag{4.67}$$

$$(C^1_{\lambda\mu})_{\tau JM\to\tau'J'M'} = \left[C_{\lambda\mu} - C^0\delta_{\lambda\mu}(-1)^\lambda\right]_{\tau JM\to\tau'J'M'} \tag{4.68}$$

In terms of reduced matrix elements these components become

$$(C^0)_{\tau JM\to\tau'J'M'} = \frac{\delta_{JJ'}\delta_{MM'}}{3\hbar(2J+1)}\sum_{\tau''J''}\frac{\omega_{\tau''J'',\tau J} + \omega_{\tau''J'',\tau'J'}}{(\omega_{\tau''J'',\tau J}-\omega_1)(\omega_{\tau''J'',\tau'J'}+\omega_1)} \tag{4.69}$$

$$(\times)\langle\tau J\|D\|\tau''J''\rangle\langle\tau'J\|D\|\tau''J''\rangle^*$$

and

$$(C^1_{\lambda\mu})_{\tau JM\to\tau'J'M'} = \frac{(-1)^{J+J'+\lambda}}{\hbar}\sum_{\tau''J''}\langle\tau J\|D\|\tau''J''\rangle\langle\tau'J'\|D\|\tau''J''\rangle \qquad (4.70)$$

$$(x)\sum_{M''}\left\{\frac{\begin{pmatrix}J&1&J''\\-M&\lambda&M''\end{pmatrix}\begin{pmatrix}J'&1&J''\\-M'&-\mu&M''\end{pmatrix}}{\omega_{\tau''J'',\tau J}-\omega_1} + (-1)^{\lambda+\mu}\frac{\begin{pmatrix}J&1&J''\\-M&\mu&M''\end{pmatrix}\begin{pmatrix}J'&1&J''\\-M'&-\lambda&M''\end{pmatrix}}{\omega_{\tau''J'',\tau'J'}+\omega_1}\right\}$$

$$-(C^0)_{\tau JM\to\tau'JM}\,\delta_{JJ'}\,\delta_{MM'}\,\delta_{\lambda,-\mu}(-1)^{\lambda}$$

Substituting from Eqs. (4.63) and (4.66) into Eq. (4.20) and summing over M and M', one obtains

$$(\sigma_{12})_{\tau J\to\tau'J'} = \frac{\omega_1(\omega_1-\omega_{\tau'J'\to\tau J})^3}{c^4\,(2J+1)}\sum_{MM'}\left|\epsilon^1_\lambda\epsilon^2_\mu\left[C^0\delta_{\lambda,-\mu}(-1)^\lambda + C^1_{\lambda\mu}\right]_{\tau JM\to\tau'J'M'}\right|^2 \qquad (4.71)$$

Substituting from Eqs. (4.69) and (4.70) for $(C^0)_{\tau JM\to\tau'J'M'}$ and $(C^1_{\lambda\mu})_{\tau JM\to\tau'J'M'}$ one may show directly that in the sum over MM' the cross terms in the absolute square in Eq. (4.71) vanish; it follows that this equation may be written in the form

$$(\sigma_{12})_{\tau J\to\tau'J'} = (\sigma^0_{12})_{\tau J\to\tau'J'} + (\sigma^1_{12})_{\tau J\to\tau'J'} \qquad (4.72)$$

where

$$(\sigma^0_{12})_{\tau J\to\tau'J'} = \frac{\omega_1(\omega_1-\omega_{\tau'J',\tau J})^3}{c^4\,(2J+1)}\sum_{MM'}\left|\epsilon^1_\lambda\,\epsilon^2_{-\lambda}\,(C^0)_{\tau JM\to\tau'J'M'}(-1)^\lambda\right|^2 \qquad (4.73)$$

$$= \delta_{JJ'}\,\frac{\omega_1(\omega_1-\omega_{\tau'J,\tau J})^3}{c^4}\cos^2\psi\left|(C^0)_{\tau J0\to\tau'J0}\right|^2$$

and

$$(\sigma^1_{12})_{\tau J\to\tau' J'} = \frac{\omega_1(\omega_1-\omega_{\tau' J',\tau J})^3}{C^4(2J+1)} \sum_{MM'} \left| \epsilon^1_\lambda \epsilon^2_\mu (C^1_{\lambda\mu})_{\tau JM\to\tau' J' M'} \right|^2$$

(4.74)

$$= \frac{\omega_1(\omega_1-\omega_{\tau' J',\tau J})^3}{C^4(2J+1)} \left\{ \cos^2\psi \sum_{M} \left|(C^1_{00})_{\tau JM\to\tau' J' M'}\right|^2 + \sin^2\psi \sum_{MM'} \left|(C^1_{01})_{\tau JM\to\tau' J' M'}\right|^2 \right\}$$

The angular dependences are easily obtained by choosing the coordinate system so that the z-axis is parallel to $\underline{\epsilon_1}$ and so that $\underline{\epsilon_2}$ lies in the xz-plane. In order to obtain Eq. (4.74), we have used the relationship

$$\sum_{MM'} \left|(C^1_{01})_{\tau JM\to\tau' J' M'}\right|^2 = \sum_{MM'} \left|(C^1_{0-1})_{\tau JM\to\tau' J' M'}\right|^2$$

Introducing the notation

$$(Q^0)_{\tau J\to\tau' J'} = \delta_{JJ'} \left|(C^0)_{\tau J0\to\tau' J0}\right|^2 \qquad (4.75)$$

$$(Q^1_0)_{\tau J\to\tau' J'} = \frac{1}{2J+1} \sum_{M} \left|(C^1_{00})_{\tau JM\to\tau' J' M}\right|^2 \qquad (4.76)$$

and

$$(Q^1_1)_{\tau J\to\tau' J'} = \frac{1}{2J+1} \sum_{MM'} \left|(C^1_{01})_{\tau JM\to\tau' J' M'}\right|^2 \qquad (4.77)$$

one obtains from Eqs. (4.72), (4.73) and (4.74)

$$(\sigma_{12})_{\tau J\to\tau' J'} = \frac{\omega_1(\omega_1-\omega_{\tau' J',\tau J})^3}{C^4} \qquad (4.78)$$

$$(\times)\left\{ \cos^2\psi \left[(Q^0)_{\tau J\to\tau' J'} + (Q^1_0)_{\tau J\to\tau' J'} - (Q^1_1)_{\tau J\to\tau' J'} \right] + (Q^1_1)_{\tau J\to\tau' J'} \right\}$$

From Eq. (4.78) a connection between the quantum expressions for the Rayleigh scattering cross section and the refractive index may be established. For particles in an initial level τJ which is degenerate only in M, the Rayleigh scattering cross section is given by $(\sigma_{12})_{\tau J \to \tau J}$ which, from Eqs. (4.78) and (4.75), involves

$$(C^0)_{\tau J 0 \to \tau J 0} = \frac{2}{3\hbar(2J+1)} \sum_{\tau'' J''} \frac{\omega_{\tau'' J'', \tau J}}{\omega^2_{\tau'' J'', \tau J} - \omega_1^2} \left| \langle \tau J \| D \| \tau'' J'' \rangle \right|^2 \qquad (4.79)$$

On the other hand a well known quantum expression for the refractive index becomes for particles in initial states degenerate only in M[60,63]

$$n^2 - 1 = \frac{8\pi}{\hbar} \eta \frac{1}{2J+1} \sum_{\tau'' J''} \frac{\omega_{\tau'' J'', \tau J}}{\omega^2_{\tau'' J'', \tau J} - \omega_1^2} \sum_{MM'} \left| \langle \tau J M | D_z | \tau J M \rangle \right|^2$$

$$(4.80)$$

$$= \frac{8\pi}{3\hbar} \eta \frac{1}{2J+1} \sum_{\tau'' J''} \frac{\omega_{\tau'' J'', \tau J}}{\omega^2_{\tau'' J'', \tau J} - \omega_1^2} \left| \langle \tau J \| D \| \tau'' J'' \rangle \right|^2$$

where η is the particle density. Substituting from this equation into Eq. (4.79) for the sum over τ"J", one obtains

$$(C^0)_{\tau J 0 \to \tau J 0} = \frac{1}{4\pi \eta} (n^2 - 1) \qquad (4.81)$$

and, from Eq. (4.75)

$$(Q^0)_{\tau J \to \tau J} = \left(\frac{n^2 - 1}{4\pi \eta} \right)^2 \qquad (4.82)$$

Finally, substituting this equation into Eq. (4.78), the Rayleigh scattering cross section becomes

$$(\sigma_{12})_{\tau J\rightarrow\tau J} = \frac{\omega_1^4}{c^4}\left\{\left[\left(\frac{n^2-1}{4\pi n}\right)^2 + (Q'_0 - Q'_1)_{\tau J\rightarrow\tau J}\right]\cos^2\psi + (Q'_1)_{\tau J\rightarrow\tau J}\right\} \tag{4.83}$$

In Appendix F it is shown that

$$(Q'_0)_{\tau J\rightarrow\tau J} = \frac{4}{3}(Q'_1)_{\tau J\rightarrow\tau J} - \omega_1^2 F_{\tau J} \tag{4.84}$$

where

$$F_{\tau J} = \frac{2}{\hbar^2(2J+1)}\sum_{\tau''J''}\sum_{\tau'''J'''}\frac{|\langle\tau J\|D\|\tau''J''\rangle|^2}{\omega^2_{\tau''J'',\tau J}-\omega_1^2}\,\frac{|\langle\tau J\|D\|\tau'''J'''\rangle|^2}{\omega^2_{\tau'''J''',\tau J}-\omega_1^2} \tag{4.85}$$

$$(\times)\ \sum_S\left[W(J''1J'''1;JS)\right]^2\left[C^{11S}_{01}C^{11S}_{10}+C^{11S}_{00}C^{11S}_{1-1}\right]$$

Here W(J"1J'"1;JS) is a Racah coefficient as defined in Ref. 77, and $C^{11S}_{MM'}$ is a Clebsch-Gordan coefficient. The Clebsch-Gordan coefficients are related to the 3-J symbols by

$$C^{J_1J_2J_3}_{M_1M_2} = (-1)^{J_1-J_2+M_1+M_2}\sqrt{2J_3+1}\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & -M_1-M_2\end{pmatrix} \tag{4.86}$$

These coefficients are employed in Eq. (4.85) rather than 3-J symbols in order to retain notation similar to that of Ref. 77.

Substituting from Eq. (4.84) into Eq. (4.83) for $(Q'_0)_{\tau J\rightarrow\tau J}$, one obtains

$$(\sigma_{12})_{\tau J\rightarrow\tau J} = \frac{\omega_1^4}{c^4}\left\{\left[\left(\frac{n^2-1}{4\pi n}\right)^2 + \frac{1}{3}(Q'_1)_{\tau J\rightarrow\tau J} - \omega_1^2 F_{\tau J}\right]\cos^2\psi + (Q'_1)_{\tau J\rightarrow\tau J}\right\} \tag{4.87}$$

It is interesting to compare this result with the classical expression for the Rayleigh cross section as given by Eq. (4.34). Associating $(Q_1^1)_{\tau J\to\tau J}$ with Ω, it is apparent that the quantum and classical relationships differ because of the presence of the factor $\omega_1^2\, F_{\tau J}$ in the former. For J=0, $F_{\tau J}$, and $(Q_1^1)_{\tau J\to\tau J}$ vanish along with depolarization and the quantum and classical relationships are in agreement. For J = 1/2, $(Q_0^1)_{\tau J\to\tau J}$ vanishes and from Eq. (4.84)

$$(Q_1^1)_{\tau\frac{1}{2}\to\tau\frac{1}{2}} = \frac{3}{4}\omega_1^2 F_{\tau J} \tag{4.88}$$

For this special case Eq. (4.83) can be put into the form

$$(\sigma_{12})_{\tau J\to\tau J} = \frac{\omega_1^4}{c^4}\left(\frac{n^2-1}{4\pi n}\right)^2\left[(1-\rho)\cos^2\psi+\rho\right] \tag{4.89}$$

Eq. (4.89) differs from the classical expression given by Eq. (4.36) in that it does not contain the factor $3/3-4\rho$. The calculations of scattering cross sections for cesium atoms which are presented in Section 4.4 indicate that this factor can differ considerably from unity over broad spectral regions. Thus it appears that there can be substantial disagreement between the quantum and classical equations for the Rayleigh cross section in terms of the refractive index. This disagreement is evident from Table 4.1, where refractive indices for a gaseous system of ground state cesium atoms as calculated from Eqs. (4.36) and (4.89) are compared.

For $J > 1/2$ both $F_{\tau J}$ and $(Q_1^1)_{\tau J \to \tau J}$ will be nonzero in general. Both of these quantities depend on the relative magnitudes of the reduced matrix elements which must be calculated for each type of scattering particle. Whenever $3\omega_1^2 F_{\tau J}$ is significant in comparison with $(Q_1^1)_{\tau J \to \tau J}$ the depolarization correction to the classical relationship between the Rayleigh scattering cross section and the refractive index, for example the factor $3/(3-4\rho_0)$ in Eq. (4.36), will differ significantly from the corresponding quantum factor.

Over the past fifty years, many light scattering experiments which involve comparisons of refractive indices and scattering cross sections have been reported.* However these comparisons do not suffice to establish the significance of the "quantum correction" $F_{\tau J}$. One problem is that most light scattering experiments involve incident beams of broad frequency distribution, whereas $F_{\tau J}$ probably depends sensitively on frequency and, for $J > 1/2$, can assume both positive and negative values. Another problem is that experimental determination of an

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*For example see Refs. 14, 24, 61, 78.

absolute light scattering cross section is quite difficult and subject to large errors. Most of the comparisons just mentioned agree with the classical relationship between cross section and refractive index to within 10%. One set of experiments reported by Vaucouleurs[78] obtains agreement within 1%. These results suggest that the "quantum correction" may be small away from resonance in the visible spectrum.

A remark concerning the definition of $\underline{\hat{J}}$ is in order at this point. This operator has been defined as the total angular momentum operator for the particle in question. However, it appears that in many cases certain contributions to the total angular momentum which couple weakly to the electron angular momentum may be neglected in calculating light scattering cross sections and depolarization. This argument is developed in Section 4.4, where the neglect of the spin of the cesium nucleus in calculating cross sections away from resonance is discussed.

4.4. CALCULATION OF RAYLEIGH SCATTERING CROSS SECTIONS FOR CESIUM ATOMS

In this section the calculation of Rayleigh scattering cross sections for cesium atoms in ground states is discussed and results presented for incident wavelengths from 6000 to 10,000 Å. This calculation is used to illustrate some of the general properties of the relevant equations.

The ground states of cesium are represented by the designation $6S_{1/2}$ having a total (electronic) angular momentum $J = 1/2$. From selection rules on J for dipole transitions, the intermediate levels which contribute to the scattering are characterized by J" = 1/2 and J" = 3/2; these are the only values of J" for which the relevant 3-J symbols are nonzero. Substituting the numerical values of these symbols into Eqs. (4.59) and (4.60) and summing over M and M', one obtains

$$(\sigma_{zz})_{\tau\frac{1}{2}\to\tau\frac{1}{2}} = \omega_1^4\left(\frac{e^2}{mc^2}\right)^2\left|\sum_{\tau''}\left\{\frac{f_{\tau''\frac{1}{2}\to\tau\frac{1}{2}}}{\omega^2_{\tau''\frac{1}{2},\tau\frac{1}{2}}-\omega_1^2}+\frac{f_{\tau''\frac{3}{2}\to\tau\frac{1}{2}}}{\omega^2_{\tau''\frac{3}{2},\tau\frac{1}{2}}-\omega_1^2}\right\}\right|^2 \tag{4.90}$$

$$(\sigma_{zx})_{\tau\frac{1}{2}\to\tau\frac{1}{2}} = \omega_1^4\left(\frac{e^2}{mc^2}\right)^2\left|\sum_{\tau''}\left\{\frac{f_{\tau''\frac{1}{2}\to\tau\frac{1}{2}}}{\omega^2_{\tau''\frac{1}{2},\tau\frac{1}{2}}-\omega_1^2}\,\frac{\omega_1}{\omega_{\tau''\frac{1}{2},\tau\frac{1}{2}}}-\frac{1}{2}\,\frac{f_{\tau''\frac{3}{2}\to\tau\frac{1}{2}}}{\omega^2_{\tau''\frac{3}{2},\tau\frac{1}{2}}-\omega_1^2}\,\frac{\omega_1}{\omega_{\tau''\frac{3}{2},\tau\frac{1}{2}}}\right\}\right|^2 \tag{4.91}$$

The cross sections calculated from these equations are plotted in Fig. 4.3. The corresponding depolarization is plotted in Fig. 4.4. The contributions of all significant bound intermediate states are included in the calculations, whereas the contributions associated with intermediate states in the positive energy continuum are not included. The latter do not appear to be significant in the frequency range of present interest. Theoretical oscillator strengths values obtained by Stone[79] are employed in these calculations. Stone's results compare well with the recent measurements of Kvater and Meister.[80]

From Fig. 4.3 it appears that the Rayleigh scattering cross section for ground state cesium atoms is large over wide spectral regions compared with the Rayleigh cross sections for most atoms and simple molecules, which are on the order of 10^{-28} cm^2. From Fig. 4.4 strong depolarization is present in spite of the fact that the cesium ground states have spherically symmetric charge distributions. This apparent

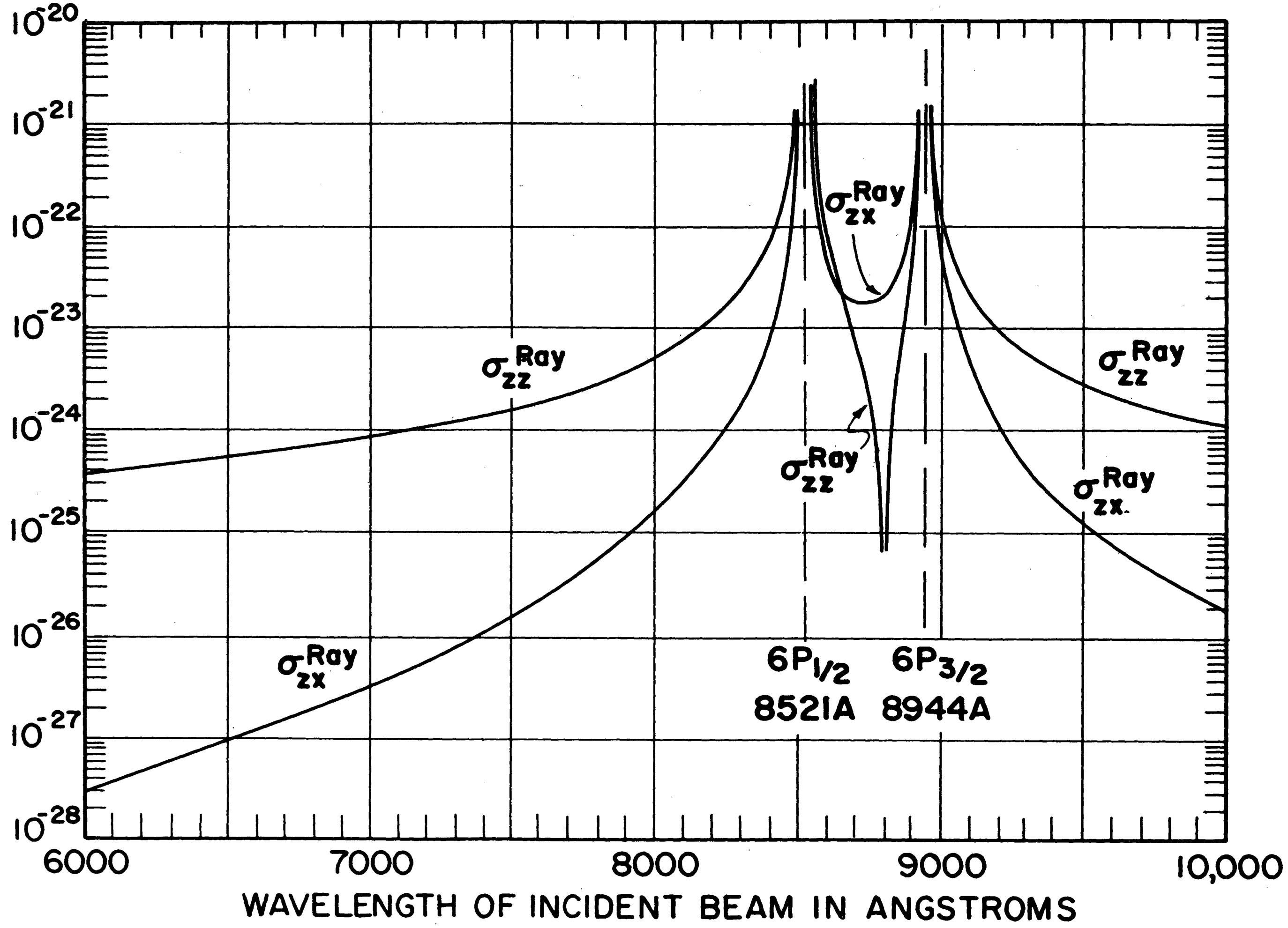

Fig. 4.3. Rayleigh scattering cross sections for cesium atoms in ground states. The vertical dashed lines denote points of resonance with $6P_{1/2}$ and $6P_{3/2}$ excited states.

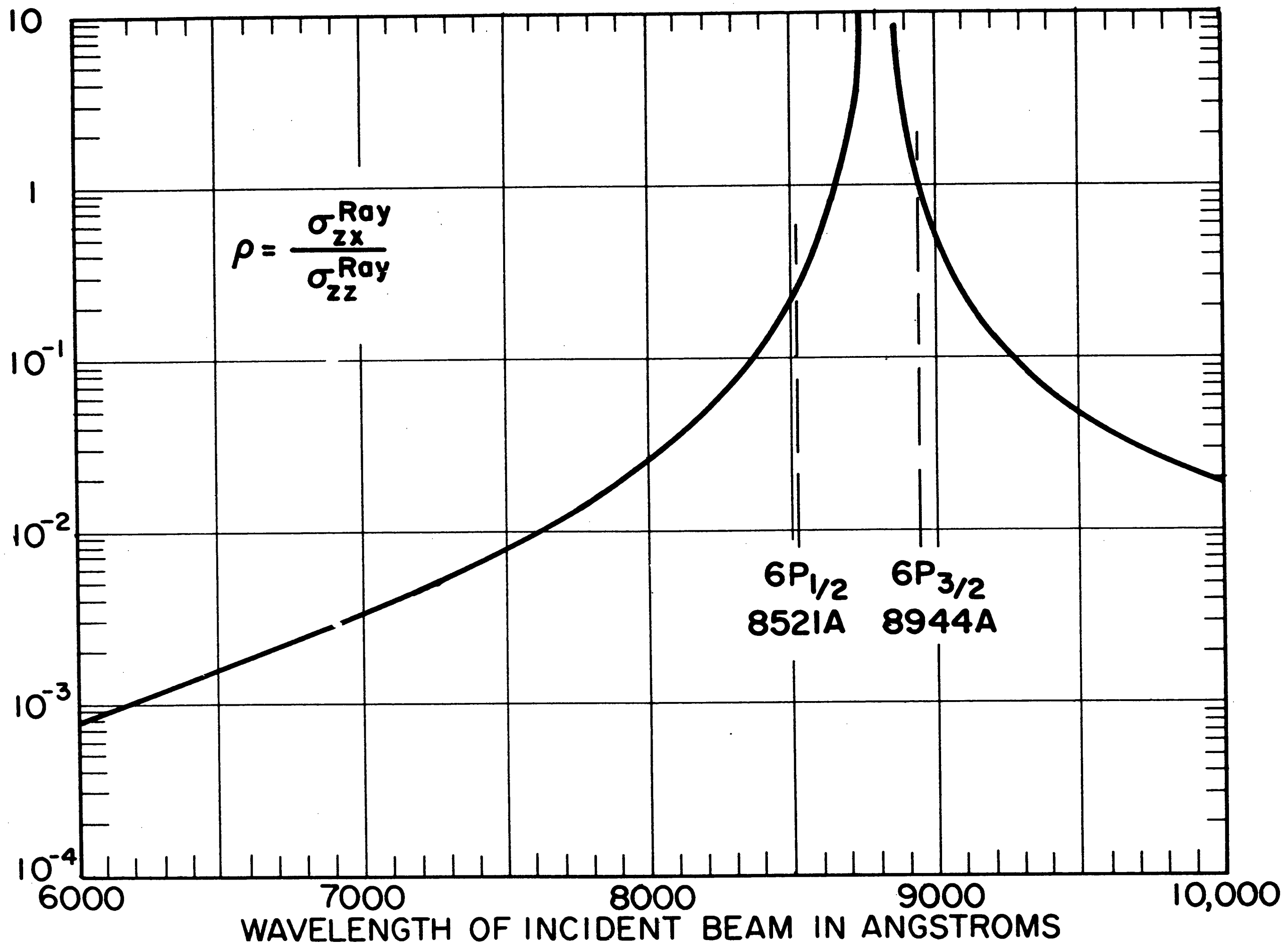

Fig. 4.4. Normal depolarization for Rayleigh scattering from cesium atoms in ground states. The vertical dashed lines denote points of resonance with $6P_{1/2}$ and $6P_{3/2}$ excited states.

paradox is discussed in Section 4.5.

Calculated values for the refractive index for wavelengths from 8000 Å to 10,000 Å are listed in Table 4.1. These values are obtained from the cross sections as plotted in Fig. 4.3 and the quantum and classical relations between the refractive index and Rayleigh scattering cross section given by Eqs. (4.89) and (4.36), respectively. The extent of the disagreement between these relations for the special case of ground state cesium atoms is evident from the table.

From the forms of Eqs. (4.90) and (4.91) it appears that contributions to σ_{ZZ} and σ_{ZX} from different intermediate states may interfere within the absolute square. Indeed the interference between J" = 1/2 and J" = 3/2 terms causes σ_{ZZ} to fall off in between the corresponding resonance points, whereas it causes σ_{ZX} to decrease rapidly outside the resonance points. If the spin orbit interactions were neglected, then the oscillator strengths $f_{\tau''1/2,\tau 1/2}$ and $f_{\tau''3/2,\tau 1/2}$ would be in the ratio 1:2, $\omega_{\tau''1/2,\tau 1/2}$ would equal $\omega_{\tau''3/2,\tau 1/2}$, and it is evident from Eq. (4.91) that σ_{ZX} would vanish because of destructive interference between the J" = 1/2 and J" = 3/2 contributions. The spin orbit interaction introduces depolarization by

a) introducing energy shifts such that $\omega_{\tau''3/2,\tau 1/2} \neq \omega_{\tau''1/2,\tau 1/2}$, and

b) changing the ratio of oscillator strengths.

Each effect tends to remove the complete destructive interference. Effect (a) is significant at separation from resonance comparable to or

TABLE 4.1

REFRACTIVE INDICES FOR CESIUM ATOMS IN GROUND STATES IN A GASEOUS SYSTEM

(These indices are calculated from the Rayleigh cross sections plotted in Fig. 4.3 and the quantum and classical relations between the Rayleigh cross section and refractive index given by Eqs. (4.89) and (4.36), respectively. The wavelength intervals are varied to bring out the details of the wavelength dependence. Blank spaces have been left where the classical relation yields an imaginary value for $n^2 - 1$.)

λ_1 Angstroms	$\frac{n^2-1}{4\pi\mathcal{N}}$ from Eq. (4.89)	$\frac{n^2-1}{4\pi\mathcal{N}}$ from Eq. (4.36)	λ_1 Angstroms	$\frac{n^2-1}{4\pi\mathcal{N}}$ from Eq. (4.89)	$\frac{n^2-1}{4\pi\mathcal{N}}$ from Eq. (4.36)
8000	-3.95×10^{-22}	-3.87×10^{-22}	8900	-1.78×10^{-21}	
8200	-6.32×10^{-22}	-6.13×10^{-22}	8920	-3.75×10^{-21}	
8400	-1.58×10^{-21}	-1.46×10^{-21}	8940	-2.81×10^{-20}	
8500	-8.46×10^{-21}	-7.18×10^{-21}	8950	1.58×10^{-20}	
8510	-1.59×10^{-20}	-1.33×10^{-20}	8960	6.48×10^{-21}	
8530	1.94×10^{-20}	1.56×10^{-20}	8970	4.20×10^{-21}	8.38×10^{-22}
8550	5.85×10^{-21}	4.49×10^{-21}	8980	3.13×10^{-21}	1.18×10^{-21}
8600	1.97×10^{-21}	1.15×10^{-21}	9000	2.17×10^{-21}	1.19×10^{-21}
8620	1.51×10^{-21}	6.23×10^{-22}	9100	9.87×10^{-22}	8.12×10^{-22}
8630	1.34×10^{-21}	1.12×10^{-22}	9200	6.89×10^{-22}	6.24×10^{-22}
8730	4.20×10^{-22}		9500	4.07×10^{-22}	3.95×10^{-22}
8780	1.14×10^{-22}		10,000	2.62×10^{-22}	2.59×10^{-22}
8830	-2.63×10^{-22}				

less than the spin orbit splitting of the corresponding intermediate level. This effect accounts for the strong depolarization around 6800 Å in Fig. 4.4. On the other hand, effect (b), where significant, contributes to depolarization over broader frequency ranges. Both effects are present in the depolarization arising from the higher excited levels of cesium. Thus the spin orbit depolarization is not strictly a resonance phenomenon.

Up to this point the possibility that nuclear spin might introduce depolarization has not been considered. Initially, for simplicity, we discuss this possibility for an atom with vanishing electron angular momentum in the initial and final states, but with nonvanishing nuclear spin, such as He^3 or Xe 131. Because of the selection rule $\Delta M = \pm 1$ on σ_{zx}, depolarization arises in Rayleigh scattering from this type of atom only if the nuclear angular momentum is reoriented during the scattering transition. This possibility may be examined by introducing into Eq. (4.91) state functions for the whole atom (including the nucleus) which are also eigenfunctions of the total atomic angular momentum (electron plus nuclear angular momentum) operator $\hat{J}^2$ and $\hat{J}_z$ Then noting that the nuclear spin interacts with the electron angular momentum through a hyperfine interaction, splitting the intermediate states, depolarization is introduced through effect (a) of the previous paragraph. The hyperfine interaction does not appear to change ratios of oscillator strengths significantly (in contradistinction to the electron spin orbit interaction); in this case the nuclear spin introduces significant depolarization only within separation from resonance comparable to the hyperfine splitting. It appears that this conclusion applies to scattering from cesium atoms, such that depolarization arising from the spin of the cesium nucleus (7/2) should be negligible in comparison to the spin orbit splitting at separations from resonance large compared with the hyperfine splitting of corresponding excited levels (a small fraction of an angstrom).

Placzek[34] has discussed briefly the depolarization arising from the hyperfine interaction, citing as an example the Hg 2537 line. If a beam of light which is constant in intensity over the 2537 Å level is passed through mercury vapor, five sharp, closely spaced lines appear in the spectrum of the scattered radiation as the result of resonance Rayleigh scattering through the five hyperfine components of the corresponding intermediate level. Placzek notes that Mitchell[81] has calculated the depolarization of each line, and Ellett and McNair,[82] Keussler,[83] Olson,[84] and Larrick and Heydenburg[85] have obtained experimental results which agree fairly well with the calculations.

The nuclear spin has one other significant effect on Rayleigh scattering from cesium. Because of the resulting hyperfine splitting of the cesium ground level, part of the "Rayleigh scattering" is actually shifted slightly from the incident frequency. However, this shift is so small (about 0.15 Å) that it would be difficult to resolve under typical experimental conditions.

4.5. DEPOLARIZATION AND THE SYMMETRY CHARACTERISTICS OF THE SCATTERING PARTICLES

In this section we redevelop a basic selection rule for various components of the scattering tensor which is based on the symmetry properties of the scattering particles, and then show that this selection rule does not exclude depolarization of light scattered from particles with spherically symmetric charge distributions in initial and final states.

In order to develop the selection rule it is convenient to express the scattering tensor $(C_{ij})_{\beta\to\beta'}$ in the form of a single matrix element. From Eq. (4.16) this tensor is represented by the components

$$(C_{j\ell})_{B\beta\to B'\beta'} = \frac{1}{\hbar}\sum_{B''\beta''}\left\{\frac{\langle B\beta|D_j|B''\beta''\rangle\langle B''\beta''|D_\ell|B\beta\rangle}{\omega_{B''B}-\omega_1} + \frac{\langle B\beta|D_\ell|B''\beta''\rangle\langle B''\beta''|D_j|B\beta\rangle}{\omega_{B''B}+\omega_1}\right\} \tag{4.92}$$

Here B designates a particular level and β, a particular state within this level. The dependence of the scattering tensor on intermediate states may be expressed in another form by introducing the projection operator P_B which is defined such that

$$\begin{aligned} P_B|B\beta\rangle &= |B\beta\rangle \quad \text{for all states } \beta \text{ in the level B} \\ P_B|B'\beta'\rangle &= 0\ , \quad B'\neq B \end{aligned} \tag{4.93}$$

This operator may be written in various forms as a functional of the Hamiltonian $\mathcal{H}$ which operates on the state functions $|B\beta\rangle$ such that

$$\mathcal{H}|B\beta\rangle = E_B|B\beta\rangle$$

For example

$$P_B = \prod_{B' \neq B} \left(\frac{\mathcal{H} - E_{B'}}{E_B - E_{B'}}\right) \qquad (4.94)$$

clearly satisfies the property (4.93). Another form which may be more convenient for certain purposes is

$$P_B = \lim_{S\to\infty} \frac{1}{S} \int_{-S/2}^{S/2} d\tau\, e^{i\tau(\mathcal{H} - E_B)} \qquad (4.95)$$

Utilizing the property (4.93) of P_B, Eq. (4.91) can be written

$$(C_{jl})_{B\beta\to B'\beta'} = \frac{1}{\hbar} \sum_{B'''} \sum_{B''\beta''} \left\{ \frac{\langle B\beta| D_j P_{B'''} | B''\beta''\rangle\langle B''\beta''| D_l |B'\beta'\rangle}{\omega_{B'''B} - \omega_1} + \frac{\langle B\beta| D_l P_{B'''} | B''\beta''\rangle\langle B''\beta''| D_j | B'\beta'\rangle}{\omega_{B'''B'} + \omega_1} \right\} \qquad (4.96)$$

The sum over B"β" may now be performed directly, employing the closure property of the functions |B"β"> to obtain

$$(C_{jl})_{B\beta\to B'\beta'} = \langle B\beta| \hat{C}_{jl} | B'\beta'\rangle. \qquad (4.97)$$

where

$$(C_{jl})_{B\beta\to B'\beta'} = \frac{1}{\hbar} \sum_{B''} \left\{ \frac{D_j P_{B''} D_l}{\omega_{B''B} - \omega_1} + \frac{D_l P_{B''} D_j}{\omega_{B'B'} + \omega_1} \right\} \qquad (4.98)$$

Definite selection rules can be developed for the matrix element*

$$\langle B\beta|\, \hat{C}_{J\ell}\, |B'\beta'\rangle = \int d\tau\, \psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B\beta} \tag{4.99}$$

from the following argument. The integral on the right hand side is invariant under any point transformation T (such as rotation or reflection about a point, reflection about a plane, etc.) which operates only on integration variables; i.e.,

$$\int d\tau\, \psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B'\beta'} = \int d\tau\, T\left[\psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B'\beta'}\right] \tag{4.100}$$

For any transformation such that

$$T\left[\psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B'\beta'}\right] = t\, \psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B'\beta'} \tag{4.101}$$

where t is a number, we have from Eq. (4.100)

$$(1-t)\int d\tau\, \psi^{*}_{B\beta}\, \hat{C}_{J\ell}\, \psi_{B'\beta'} = 0 \tag{4.102}$$

If $t \neq 1$, then obviously the integral must vanish. For example consider the point transformation Π which represents reflection through a point. For state functions of definite parity we have

$$\Pi\psi = \pm\psi$$

If $\Pi\mathcal{H} = \mathcal{H}$ then from Eq. (4.94) or (4.95), $\Pi\, P_B = P_B$ and

---

*The notation $\int d\tau$ in Eq. (4.99) implies a sum over discrete spin coordenotes as well as an integral over continuous position coordinates.

$$\Pi \hat{C}_{j\ell} = \hat{C}_{j\ell}$$

Then if the states $\psi_{B\beta}$ and $\psi_{B'\beta'}$ have opposite parity

$$\Pi\left[\psi^*_{B\beta}\, \hat{C}_{j\ell}\, \psi_{B'\beta'}\right] = -\psi^*_{B\beta}\, \hat{C}_{j\ell}\, \psi_{B'\beta'}$$

and the integral must vanish. Note that for the group of all symmetry operations which leave $\mathcal{H}'$ invariant, $\hat{C}_{j\ell}$ transforms like D_jD_ℓ. It follows that if the integral

$$\int d\tau\, \psi^*_{B\beta}\, D_j D_\ell\, \psi_{B'\beta'} \qquad (4.103)$$

can be shown to vanish using a transformation *belonging to the symmetry group of $\mathcal{H}$*, then C_{ij} must vanish also. Placzek[34] has developed detailed symmetry selection rules based on this relationship between (4.99) and (4.103) in his extensive work on the application of group theory to light scattering. However, it ought to be emphasized that for the purpose of determining selection rules for $(C_{j\ell})_{B\beta\to B'\beta'}$ from Eq. (4.103), one should use only point symmetry transformations belonging to the symmetry group $\mathcal{G}$ of the Hamiltonian $\mathcal{H}$. If Eq. (4.97) is shown to vanish using a transformation not contained in $\mathcal{G}$, it does not follow that $(C_{j\ell})_{B\beta\to B'\beta'}$ must vanish. A good example of this point is presented in Rayleigh scattering from ground state cesium atoms. According to the results of Section 4.2, depolarization arises from the scattering tensor component $(C_{zx})_{\beta B\to B'\beta'}$. On the other hand we may show that

$$\int d\tau \, \psi^{*}_{B\beta} D_z D_x \psi_{B\beta'} = 0$$

by reflecting the electron position coordinates about the yz-plane, noting that the ground states $\psi_{B\beta}$ and $\psi_{B\beta'}$ are invariant in this transformation and D_zD_x changes sign. However, this result does not imply that $(C_{zx})_{B\beta \to B'\beta'}$ vanishes, since the spin-orbit contribution to $\mathcal{H}$ changes under this reflection (and other any other transformation which may be used to show that the integral vanishes). Thus the symmetry theory does not contradict the results of Section 4.4.

CHAPTER V

CONCLUSION

There seem to be several possibly interesting extensions of the theoretical results obtained in previous chapters. Also several experiments are suggested. These are discussed in this chapter.

In Section 1.1 terms arose in the second-order contribution to the scattering cross section which correspond to scattering events in which two particles change state simultaneously. Of course if third-order contributions had been considered, terms in which three particles change state would arise, etc. There is a tendency to ignore such contributions on the grounds that they are "nonphysical." We show in Appendix C that these terms vanish in the ideal gas approximation, and in a real gas they have a strong resonance character. It is possible that these terms might be significant for scattering near resonance in sufficiently dense scattering systems. Both experimental and theoretical investigations of this possibility appear accessible and might be of interest.

The possible dependence of the scattering on the dimensions of the incident beam and scattering volume mentioned in Section 1.5 might be investigated through such methods as those developed by Osborn[57] and Klevans.[58] Using the relatively powerful single mode gas lasers now available, the scattering from volumes with dimensions on the order of a micron ought to be observable. In liquids and solids the scattering from such a small volume might be considerably more intense because of diminution of destructive interference. Such scattering might reveal interesting properties of the medium. In gases this type of experiment might be used to check Theimer's suggestion[59] that the scattering in a gas depends on the shape of the scattering volume if the volume is sufficiently small.

From Chapter II and Appendix D, it appears that the expression of the scattering cross section in terms of Van Hove G-functions fails near resonance. Likewise, the expression of the cross section integrated over final frequency in terms of the single time correlation functions $g(\rho_-)$ fails at resonance. Using methods similar to those introduced in Appendix D, in the ideal gas approximation one may still sum over intermediate external states, obtaining subsequent expressions for the resonance scattering cross sections in terms of modified correlation functions. In a real gas the situation is more complicated because the energy of the intermediate external state is no longer determined by the initial external state through the matrix element $<\mathcal{B}''|e^{i\underline{k}\cdot\underline{R}}|\mathcal{B}>$. However, meaningful results might still be obtained through appropriate approximations. Noting that resonance scattering is an important mechanism in stellar atmospheres, strongly affecting radiation transport, it appears that the formulation of resonance scattering cross sections in terms of modified correlation functions might be of considerable interest to astrophysicists. This formulation might complement other methods of examining resonance scattering such as those developed by Spitzer.

The calculations presented in Section 4.4 indicate that the light Rayleigh-scattered from ground state cesium atoms will show strong depolarization for incident wavelengths near 8800 Å. In fact, the normal depolarization is greater than one over a spectral range greater than 100 Å. This indication of strong depolarization is in disagreement with the results of classical theory which, for separation from resonance which is large compared to line widths, predicts a maximum value of 1/3 for normal depolarization.[23] Experimental investigation of the depolarization would appear to be of considerable interest because if it is observed to be as large as predicted in Section 4.4, then the classical theory will be contradicted under conditions for which it was thought to be valid.

Both experimental and theoretical examination of the descrepancy between the quantum and classical expressions for Rayleigh scattering cross sections in terms of refractive indices and depolarization, contained in the factor F_{TJ} in Eq. (4.85), would be of interest. We note that the magnitude of F_{TJ} depends on the relative magnitudes of the reduced matrix elements involved. In the case of ground state cesium atoms the reduced matrix elements may be calculated from oscillator strengths and the factor F_{TJ} is seen to be quite large. Experimental verification of this result seems to be indicated.

Finally, it is probably true that many of the results obtained for gases and plasma systems in this dissertation may have broader application. In particular, the results of Chapter II appear to be applicable in the presence of slow varying or constant external fields and in solids or liquids. Conversely, the results of Chapter IV are not obviously applicable under these conditions because it has been assumed that the scattering particles are freely oriented and to a large extent coherent interference scattering has been ignored. It is not difficult to modify the results of Chapter IV to take coherent interference scattering into account. The effects of slowly varying or constant electric or magnetic fields are not so easily included.

APPENDIX A

CENTER-OF-MASS TRANSFORMATIONS

In Section 1.1 it is noted that the Hamiltonian for a single particle

$$\mathcal{H}^M_\alpha = \sum_j^{Z_\alpha} \frac{\left(\underline{p}_{\alpha j} - \frac{e_j}{c}\underline{A}_{\alpha j}\right)^2}{2m_{\alpha j}} + V_\alpha \tag{A.1}$$

may be broken up into three parts: one describing the motion of the center of mass of the particle; one describing motions of electrons and nuclei about the center of mass; and one describing the interactions between the particles and radiation fields. For the purposes of Hamiltonian classical mechanics and quantum mechanics it is often convenient to require that the transformation be canonical.[86] Here we discuss one such transformation.

A center-of-mass transformation which is convenient for atoms is defined by

$$\underline{R}_\alpha \equiv \frac{1}{M_\alpha}\left[M_{\alpha 0}\underline{r}_{\alpha 0} + \sum_j^Z m\,\underline{r}_{\alpha j}\right] \tag{A.2}$$

$$\underline{\rho}_{\alpha j} \equiv \underline{r}_{\alpha j} - \underline{r}_{\alpha 0} \tag{A.3}$$

where M_α is the total mass of the particle, $M_{\alpha 0}$ is the mass of the nucleus, and m is the electronic mass. The nucleus is located at $\underline{r}_{\alpha 0}$ and the j^{th} of Z_α electrons at $\underline{r}_{\alpha j}$. This transformation has the inverse

$$\underline{r}_{\alpha 0} = \underline{R}_{\alpha} - \frac{1}{M}\sum_{j=1}^{Z} m\underline{\rho}_{\alpha j} \tag{A.4}$$

$$\underline{r}_{\alpha j} = \underline{\rho}_{\alpha j} + \underline{R}_{\alpha} - \frac{1}{M}\sum_{l=1}^{Z} m_{\alpha}\underline{\rho}_{\alpha l} \quad , \; j \neq 0 \tag{A.5}$$

The momentum operator transforms like

$$-i\hbar\frac{\partial}{\partial r_{\alpha j\mu}} = -i\hbar\frac{\partial R_{\alpha\nu}}{\partial r_{\alpha j\mu}}\frac{\partial}{\partial R_{\alpha\nu}} - i\hbar\sum_{l=1}^{Z}\frac{\partial \rho_{\alpha l\nu}}{\partial r_{\alpha j\mu}}\frac{\partial}{\partial \rho_{\alpha j\mu}} \tag{A.6}$$

Here subscripts μ and ν denote vector components. For j=0 one obtains

$$p_{\alpha 0\mu} = \frac{m}{M}P_{\alpha\mu} + \sum_{j=1}^{Z}\pi_{\alpha j\mu} \tag{A.7}$$

and for j≠0,

$$p_{\alpha j\mu} = \frac{m}{M}P_{\alpha\mu} + \pi_{\alpha\mu} \tag{A.8}$$

where the operators $P_{\alpha\mu}$ and $\pi_{\alpha\mu}$ are defined by

$$P_{\alpha\mu} = -i\hbar\frac{\partial}{\partial R_{\alpha\mu}} \tag{A.9}$$

$$\pi_{\alpha j\mu} = -i\hbar\frac{\partial}{\partial \rho_{\alpha j\mu}} \tag{A.10}$$

Substituting Eqs. (A.9) and (A.10) into Eq. (A.1) one obtains

$$\mathcal{H}^{\alpha} = \frac{P_{\alpha}^{2}}{2M_{\alpha}} - \frac{e_{\alpha 0}}{M_{\alpha}C}\underline{A}_{\alpha 0}\cdot\underline{P}_{\alpha} + \sum_{j}^{Z_{\alpha}}\frac{e}{M_{\alpha}C}\underline{A}_{\alpha j}\cdot\underline{P}_{\alpha} + \frac{e_{\alpha 0}^{2}}{2M_{\alpha 0}C^{2}}A_{\alpha 0}^{2}$$

$$+\sum_{j=1}^{Z_\alpha}\left\{\frac{\Pi_{\alpha j}^{2}}{2\mu_\alpha}+\left[\frac{e}{mc}\underline{A}_{\alpha j}-\frac{e_{\alpha 0}}{M_{\alpha 0}c}\underline{A}_{\alpha 0}\right]\cdot\underline{\Pi}_{\alpha j}+\frac{e^{2}}{2mc^{2}}A_{\alpha j}^{2}+\frac{1}{2M_{\alpha 0}}\sum_{l=1}^{Z_\alpha}\underline{\Pi}_{\alpha j}\cdot\underline{\Pi}_{\alpha l}\right\} \tag{A.11}$$

where

$$\mu_\alpha=\frac{M_{\alpha 0}+m}{mM_{\alpha 0}}$$

Thus we may write

$$\mathcal{H}_\alpha^{M}=H_\alpha^{MX}+H_\alpha^{N}+H_\alpha^{MR} \tag{A.12}$$

where

$$H_\alpha^{MX}=\frac{P_\alpha^{2}}{2M_\alpha} \tag{A.13}$$

$$H_\alpha^{N}=\sum_{j=1}^{Z_\alpha}\left\{\frac{\Pi_{\alpha j}^{2}}{2\mu_\alpha}+\frac{1}{2M_{\alpha 0}}\sum_{l=1}^{Z_\alpha}{}'\,\underline{\Pi}_{\alpha j}\cdot\underline{\Pi}_{\alpha l}\right\}+V_\alpha \tag{A.14}$$

$$H_\alpha^{MR}=-\frac{e_{\alpha 0}}{M_\alpha c}\underline{A}_{\alpha 0}\cdot\underline{P}_\alpha+\sum_{j=1}^{Z_\alpha}\frac{e}{mc}\underline{A}_{\alpha j}\cdot\underline{P}_\alpha+\frac{e_{\alpha 0}^{2}}{2M_{\alpha 0}c^{2}}A_{\alpha 0}^{2}+\sum_{j=1}^{Z_\alpha}\left\{\left[\frac{e}{M_\alpha c}\underline{A}_{\alpha j}-\frac{e_{\alpha 0}}{M_{\alpha 0}c}\underline{A}_{\alpha 0}\right]\cdot\underline{\Pi}_{\alpha j}+\frac{e^{2}}{2mc^{2}}A_{\alpha j}^{2}\right\} \tag{A.15}$$

To a good approximation H_α^{MR} is given by

$$H_\alpha^{MR}=\sum_{j}^{Z_\alpha}\left[\frac{e}{mc}\underline{A}_{\alpha j}\cdot\underline{\Pi}_{\alpha j}+\frac{e^{2}}{2mc^{2}}A_{\alpha j}^{2}\right] \tag{A.16}$$

A tedious but straighforward calculation reveals that the error introduced into the cross section by this approximation is on the order of $4\,\frac{Z_\alpha m}{M_{\alpha 0}}$ compared to one, or approximately 0.1%.

Similar transformations may be defined for polyatomic molecules.[87] Again it appears that H_{α}^{MR} is well approximated by Eq. (A.16).

APPENDIX B

DEPENDENCE OF THE SCATTERING CROSS SECTION ON THE WIDTHS AND SHIFTS OF INITIAL, INTERMEDIATE AND FINAL STATES

As mentioned in Chapter I, damping theory as developed by Akcasu[56] suggests a second-order approximation for the transition rate per unit time from state $|i\rangle$ to state $|f\rangle$ of the form

$$T_{i\to f} = \frac{2\pi}{\hbar}\left| V_{fi} - {\sum_{g}}' \frac{V_{fg}V_{gi}}{E_{gi} + \hbar S_{gi} - i\hbar W_{gi}} \right|^2 F_{fi}(E_{fi}) \tag{B.1}$$

$$F_{fi}(E_{fi}) = \frac{\hbar}{\pi}\,\frac{|W_{fi}|}{(E_{fi}+\hbar S_{fi})^2 + \hbar^2 W_{fi}^2} \tag{B.2}$$

Here, for example, $W_{fi} \equiv W_f - W_i$ where $\hbar W_i$ is the energy half width at half maximum associated with the state $|i\rangle$. We have from damping theory

$$\hbar W_i \cong \pi \sum_{\lambda \neq i} |V_{\lambda i}|^2 \delta(E_{\lambda i}) \tag{B.3}$$

Likewise $S_{fi} \equiv S_f - S_i$, where S_i is the energy shift assoicated with the state $|i\rangle$, given by

$$\hbar S_i \cong V_{ii} + \sum_{\lambda \neq i} \frac{|V_{\lambda i}|^2}{E_{\lambda i} + S_{\lambda i}} \tag{B.4}$$

Damping theory provides a strong argument for Eq. (B.1) for the important special case in which only the widths and shifts of intermediate states are significant. Then, noting that

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

Equation (B.1) becomes

$$T_{i\to f} = \frac{2\pi}{\hbar}\left| V_{fi} - \sum_g{}' \frac{V_{fg}V_{gi}}{E_{gi}+\hbar S_{gi}-iW_{gi}} \right|^2 \delta(E_{fi}) \qquad \text{(B.5)}$$

The arguments presently available from damping theory for Eqs. (B.1) and (B.2) seem to be much weaker for cases in which the widths of initial and final states are significant. Nevertheless, this result is reasonable from at least two standpoints. First, in the limit in which all widths and shifts vanish, Eq. (B.1) becomes equivalent to the result of ordinary perturbation theory as given by Eq. (1.34).

Second, consider a system of N particles which do not interact with each other but only with a radiation field. Then the state functions for this system may be factored into individual particle functions. It follows from Eq. (B.2) that in this case the widths, for example W_i, are given by

$$W_i = W_i^{(1)} + W_i^{(2)} + \dots + W_i^{(N)} \qquad \text{(B.6)}$$

Since each contribution is positive, if there are a large number of particles in states with finite widths, W_i also becomes very large. This quantity is extensive, i.e., it depends on the number of particles in the system. However, according to Eq. (B.1), in a scattering transition only the differences of widths are involved. If only one particle changes state in the scattering transition, then only the widths of the states of this particle remain in the differences of system widths W_{fi} and W_{gi} to affect the scattering. This result is reasonable for a system of noninteracting particles and lends support to Eq. (B.2).

For the purposes of this appendix we will assume that Eq. (B.1) provides a valid description of the effects of widths of initial and final states. The exact form of $F_{fi}(E_{fi})$, which admittedly is controversial, is not crucial to the arguments to follow.

We show here that it is possible to include the widths (and shifts) of states in the development of the scattering cross section, at least in a first approximation. The inclusion of widths of intermediate states is, perhaps, of greatest interest, because of the importance of these widths near resonance. However, we shall also include the widths of initial and final states up to the point where it is possible to evaluate their qualitative significance. The effects of these widths on the scattering may be significant in high resolution experiments,[67] where natural widths are observable, or in stellar atmospheres or some laboratory plasmas, when a considerable fraction of the particles may be in initial states with large widths.

Starting from Eq. (B.1) instead of Eq. (1.34) and following the steps of Chapters I and II through Eq. (2.1), one obtains for the scattering cross section

$$(B.7)$$

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1\rightarrow\underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{N\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{\mathcal{B}'\mathcal{B}}\sum_{b'b}P_{\mathcal{B}b}\,F_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}\left(\omega_{\mathcal{B}'\mathcal{B}}+\omega_{b'b}-\omega\right)$$

$$(x)\Bigg|(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\sum_{\gamma}^{N_e}\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{r}_\gamma}|\mathcal{B}\rangle\delta_{b'b}+\sum_{\alpha}^{N_M}Z_\alpha\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\delta_{b'b}$$

$$+\frac{1}{\hbar m}\sum_{\alpha}^{N_M}\sum_{\mathcal{B}''b''}\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}-\omega_{b''b}-S_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}+iW_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}}\right.$$

$$\left.-\frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}+\omega_{b''b}+S_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}-iW_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}}\right\}\Bigg|^2$$

where

$$\bar{}_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}(\omega) = \frac{1}{\pi}\,\frac{|W_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}|}{\left(\omega+S_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}\right)^2+\left(W_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}\right)^2} \qquad (B.8)$$

From the argument developed in Appendix C, it appears that one may sum over intermediate external states $\mathcal{B}''$ if the separation from resonance is sufficient such that, for example, $\omega_1-\omega_{b''b}$ is much greater than $\omega_{\mathcal{B}''\mathcal{B}} + S_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}-i\,W_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta}$ for all intermediate external states for which the matrix elements $<\mathcal{B}''|e^{i\underline{k}\cdot\underline{R}}|\mathcal{B}>$ are significant. However, this condition appears to be too strong, for the following reason. The intermediate external and radiation states are only slightly different than the corresponding initial states, changing only through the emission or absorption of one photon and subsequent, relatively slight recoil energy imparted to one or a few particles. Therefore to a good approximation one should have

$$S_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta} = S_{\mathcal{B}b''\eta,\mathcal{B}b\eta}$$

and (B.9)

$$W_{\mathcal{B}''b''\eta'',\mathcal{B}b\eta} = W_{\mathcal{B}b''\eta,\mathcal{B}b\eta}$$

Thus it appears that one need establish only the insignificance of $\omega_{\mathcal{B}''\mathcal{B}}$ in the denominators in order to sum directly over $\mathcal{B}''$. Note that the argument leading to Eqs. (B.9) applies also to the final state with the result that to a good approximation

$$F_{\mathcal{B}'b'\eta',\mathcal{B}b\eta}(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega) = F_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega) \qquad \text{(B.10)}$$

Substituting Eqs. (B.9) and (B.10) into Eq. (B.7) and ignoring $\omega_{\mathcal{B}''\mathcal{B}}$, the sum over $\mathcal{B}''$ leads to

$$\sigma(\underline{\epsilon}_1 \omega_1 \underline{\Omega}_1 \rightarrow \underline{\epsilon}_2 \omega_2 \underline{\Omega}_2) = \frac{1}{N} \frac{\omega_2}{\omega_1} \left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}\mathcal{B}} \sum_{b'b} P_{\mathcal{B}b} \qquad \text{(B.11)}$$

$$(\times)\ F_{\mathcal{B}b'\eta \rightarrow \mathcal{B}b\eta}(\omega_{\mathcal{B}'\mathcal{B}} + \omega_{b'b} - \omega) \left| \sum_{\alpha} \langle \mathcal{B}' | e^{i\underline{k}\cdot\underline{R}_\alpha} | \mathcal{B} \rangle (A_\alpha)_{\mathcal{B}b'\eta,\mathcal{B}b\eta} \right|^2$$

where

$$(A_\alpha)_{\mathcal{B}b'\eta,\mathcal{B}b\eta} = (\underline{\epsilon}_1 \cdot \underline{\epsilon}_2) Z_\alpha \delta_{b'b} \qquad \text{(B.12)}$$

$$+ \frac{1}{\hbar m} \sum_{b''} \left\{ \frac{\langle b' | \Pi_{\alpha 2} | b'' \rangle \langle b'' | \Pi_{\alpha 1} | b \rangle}{\omega_1 - \omega_{b''b} - S_{\mathcal{B}b''\eta,\mathcal{B}b\eta} + iW_{\mathcal{B}b''\eta,\mathcal{B}b\eta}} - \frac{\langle b' | \Pi_{\alpha 1} | b'' \rangle \langle b'' | \Pi_{\alpha 2} | b \rangle}{\omega_2 + \omega_{b''b} + S_{\mathcal{B}b''\eta,\mathcal{B}b\eta} - iW_{\mathcal{B}b''\eta,\mathcal{B}b\eta}} \right\}$$

It is convenient to introduce the Fourier transform of $F_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\omega)$ defined by

$$\Phi_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\tau) = \int_{-\infty}^{\infty} d\omega' e^{-i\omega'\tau} F_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\omega') \tag{B.13}$$

such that

$$F_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau e^{i\omega\tau}\, \Phi_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\tau) \tag{B.14}$$

Substituting Eq. (B.14) into Eq. (B.11), and multiplying out the absolute square, one obtains

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{\mathcal{B}'\mathcal{B}}\sum_{b'b} P_{\mathcal{B}b} \sum_{\alpha\alpha'} (A_\alpha)^*_{\mathcal{B}b'\eta\mathcal{B}b\eta} (A_{\alpha'})_{\mathcal{B}b'\eta,\mathcal{B}b\eta} \tag{B.15}$$

$$(x) \int d\tau e^{i(\omega_{b'b} + S_{\mathcal{B}b'\eta,\mathcal{B}b\eta} - \omega)}\, \Phi_{\mathcal{B}b'\eta,\mathcal{B}b\eta}(\tau)$$

$$(x) \langle\mathcal{B}|e^{-i\underline{K}\cdot\underline{R}_\alpha} e^{\frac{i\tau}{\hbar}H^x}|\mathcal{B}'\rangle\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_{\alpha'}} e^{-\frac{i\tau}{\hbar}H^x}|\mathcal{B}\rangle$$

We assume for simplicity that $P_{\mathcal{B}b}$ may be factored into $P_{\mathcal{B}}P_b$. Then summing over $\mathcal{B}$ and $\mathcal{B}'$, the cross sections may be put into the form

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \rightarrow \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{b'b} P_b \sum_{\alpha\alpha'} A^*_{\alpha b'b} A_{\alpha' b'b} \tag{B.16}$$

$$(x) \int d\tau e^{i(\omega_{b'b} - \omega)\tau}\, \Phi_{b'b}(\tau) \langle e^{-i\underline{K}\cdot\underline{R}_\alpha(0)} e^{i\underline{K}\cdot\underline{R}_{\alpha'}(\tau)}\rangle$$

where < > denotes an average over external states. In order to obtain Eq. (B.16), widths and shifts which depend on external states have been replaced by appropriate averages over external states. The average shifts have been incorporated into $\omega_{b'b}$ and $\omega_{b''b}$. Thus for example

$$A_{\alpha b'b} = \underline{\epsilon}_1\cdot\underline{\epsilon}_2 Z_\alpha \delta_{b'b} \tag{B.17}$$

$$+ \frac{1}{\hbar m}\sum_{b''}\left\{\frac{\langle b'|\Pi_{\alpha 2}|b''\rangle\langle b''|\Pi_{\alpha 1}|b\rangle}{\omega_1-\omega_{b''b}+iW_{b''b}} - \frac{\langle b'|\Pi_{\alpha 1}|b''\rangle\langle b''|\Pi_{\alpha 2}|b\rangle}{\omega_2+\omega_{b''b}-iW_{b''b}}\right\}$$

and

$$\Phi_{b'b}(\tau) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega\tau}\,\frac{|W_{b'b}|}{\omega^2+(W_{b'b})^2} \tag{B.18}$$

Substituting from Eq. (2.15) for $\left\langle e^{-iK\cdot R_\alpha(0)}\, e^{iK\cdot R_{\alpha'}(\tau)}\right\rangle$ one obtains

$$\sigma(\underline{\epsilon}_1\omega_1\Omega_1\rightarrow\underline{\epsilon}_2\omega_2\Omega_2) = \frac{\omega_2}{2\pi N\omega_1}\left(\frac{e^2}{mc^2}\right)^2\sum_{b'b}P_b\sum_{\alpha\alpha'}A^*_{\alpha b'b}A_{\alpha' b'b} \tag{B.19}$$

$$(\mathrm{x})\int d^3\rho\, d\tau\, e^{i[\underline{K}\cdot\underline{\rho}+(\omega_{b'b}-\omega)\tau]}\,\Phi_{b'b}(\tau)\, G_{\alpha\alpha'}(\underline{\rho},\tau)$$

The effect of widths of initial and final states may be examined qualitatively from this equation. From Eq. (B.18)

$$\int_{-\infty}^{\infty} d\tau\, \Phi_{b'b}(\tau) = \frac{2}{|W_{b'b}|}$$

$$\Phi_{b'b}(\tau) = \Phi_{b'b}(-\tau) = \Phi^*_{b'b}(\tau) \tag{B.20}$$

$$\Phi_{b'b}(0) = 1$$

These properties and the qualitative relationship between $\Phi_{b'b}(\tau)$ and $F_{b'b}(\omega)$ are illustrated in Fig. B.1. It is apparent from this figure

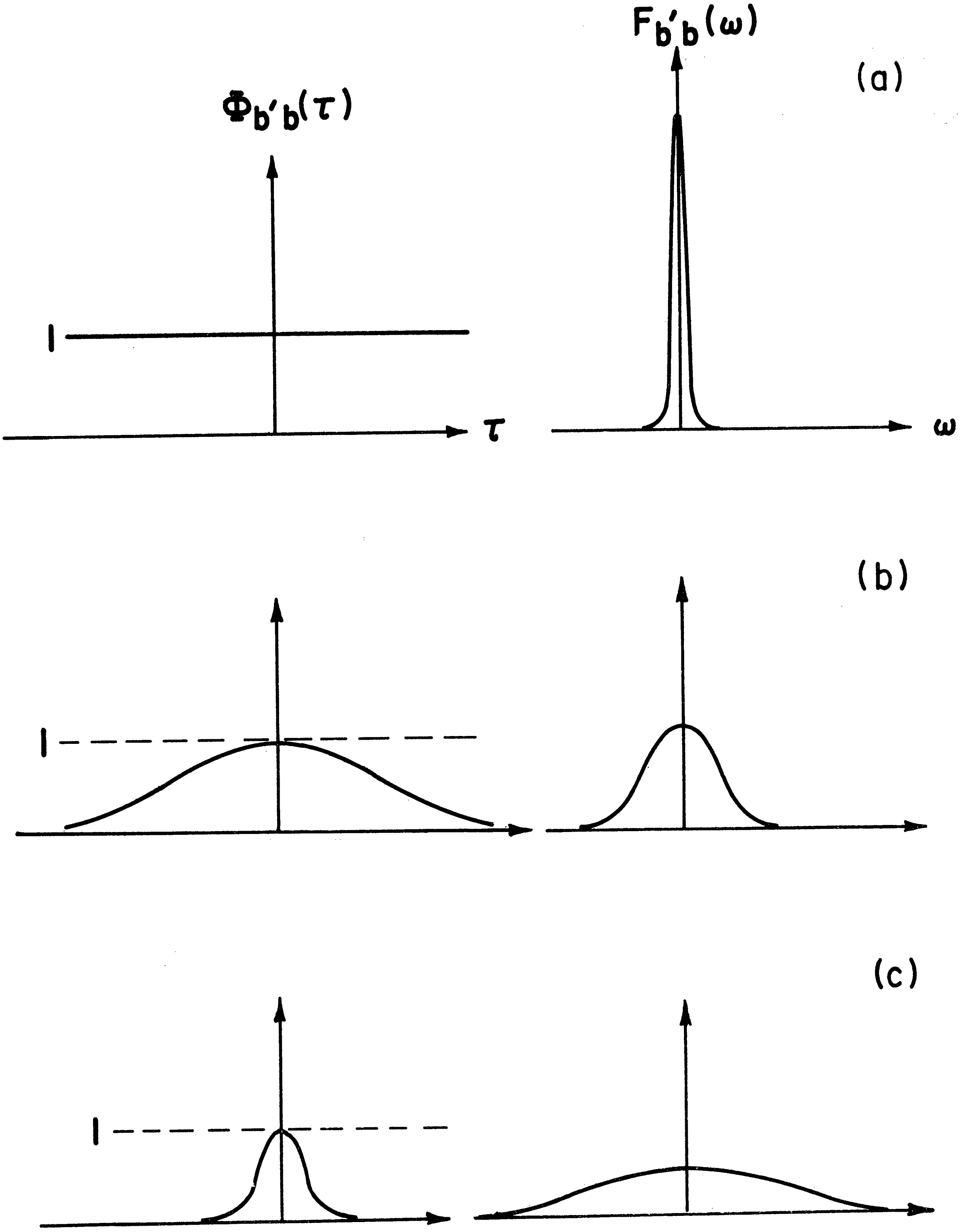

Fig. B.1. Relationship between $\Phi_{b'b}(\tau)$ and $F_{b'b}(\omega)$. The set (a) corresponds to small $W_{b'b}$, set (b), to intermediate $W_{b'b}$, and set (c) to large $W_{b'b}$.

that as $F_{b'b}(\omega)$ becomes broader, $\Phi_{b'b}(\tau)$ drops off more sharply for increasing (τ). Noting that $G_{\alpha\alpha'}(\rho_-,\tau)$ is a correlation function between particles α and α', this behavior of $\Phi_{b'b}(\tau)$ has the effect of diminishing the importance of long time correlations as $F_{b'b}(\omega)$ becomes broader.

This effect may be regarded from another viewpoint by employing a convolution theorem for Fourier transforms of the form

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} A(\tau)B(\tau) = \int_{-\infty}^{\infty} d\omega' \mathcal{A}(\omega')\mathcal{B}(\omega-\omega') \tag{B.21}$$

where, for example

$$\mathcal{A}(\omega') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} A(\tau) \tag{B.22}$$

Applying this theorem to Eq. (B.19), one obtains

$$\sigma(\underline{\epsilon}_1\omega_1\underline{\Omega}_1 \to \underline{\epsilon}_2\omega_2\underline{\Omega}_2) = \frac{\omega_2}{N\omega_1}\left(\frac{e^2}{mc^2}\right)^2 \sum_{b'b} P_b \sum_{\alpha\alpha'} A^*_{\alpha b'b} A_{\alpha' b'b} \tag{B.23}$$
$$(\times) \int d\omega' F_{b'b}(\omega') S_{\alpha\alpha'}(\underline{\kappa}, \omega_{b'b}-\omega-\omega')$$

where

$$S_{\alpha\alpha'}(\underline{\kappa},\omega) = \frac{1}{2\pi}\int d^3\rho\, d\tau\, e^{i[\underline{\kappa}\cdot\underline{\rho}-\omega\tau]} G_{\alpha\alpha'}(\underline{\rho},\tau) \tag{B.24}$$

From Eq. (B.23) it is apparent that in the convolution integral over ω' the function $F_{b'b}(\omega')$ smears or broadens the details of the frequency distribution of $S_{\alpha\alpha'}(\kappa,\omega)$. Note that neglecting line widths and shifts the function $S_{\alpha\alpha'}(\kappa,\omega_{b'b}-\omega)$ contains all of the dependence of the cross section on external states.

The notation of Eq. (B.10) implies that $F_{b'b}(\omega)$ will become $\delta(\omega)$ for coherent scattering ($b'=b$). In fact, if Eq. (B.2) for this function is valid, then this approximation is probably quite good in many cases, since for coherent scattering the initial and final internal states are the same and the slight change in external and radiation states during a scattering transition may not affect the widths and shifts significantly.

APPENDIX C

THE TRANSITION PROBABILITY

Multiplying out the various terms within the absolute square in Eq. (1.47) one obtains

$$T_{\mathcal{B}b\eta\rightarrow\mathcal{B}'b'\eta'} = \frac{2\pi}{\hbar^2}\left(\frac{e^2}{mc^2}\right)^2\left(\frac{2\pi\hbar c}{L^3}\right)^2\left[\frac{\eta_1(1+\eta_2)}{k_1k_2}\right]\delta(\omega_{\mathcal{B}'\mathcal{B}}+\omega_{b'b}-\omega) \qquad \text{(C.1)}$$

$$(X)\Bigg|\ (\underline{\epsilon}_1\cdot\epsilon_2)\sum_{j}^{N_e}\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{r}_j}|\mathcal{B}\rangle\delta_{b'b} \qquad \text{(a)}$$

$$+\frac{1}{\hbar m}\sum_{\mathcal{B}''}\sum_{jl}\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{r}_l}p_{l2}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}}\right.$$

$$\left.-\frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{r}_j}p_{j1}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{r}_l}p_{l2}|\mathcal{B}\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}}\right\}$$

$$+(\underline{\epsilon}_1\cdot\underline{\epsilon}_2)\delta_{b'b}\sum_{\alpha}Z_\alpha\langle\mathcal{B}'|e^{i\underline{K}\cdot\underline{R}_\alpha}|\mathcal{B}\rangle \qquad \text{(b)}$$

$$+\frac{1}{\hbar m}\sum_{B''}\sum_{\alpha}^{N_M}\left\{\frac{\langle\mathcal{B}'|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha2}|b''\rangle\langle b''|\Pi_{\alpha1}|b\rangle}{\omega_1-\omega_{\mathcal{B}''\mathcal{B}}-\omega_{b''b}}\right.$$

$$\left.-\frac{\langle\mathcal{B}'|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}''\rangle\langle\mathcal{B}''|e^{-i\underline{k}_2\cdot\underline{R}_\alpha}|\mathcal{B}\rangle\langle b'|\Pi_{\alpha1}|b''\rangle\langle b''|\Pi_{\alpha2}|b\rangle}{\omega_2+\omega_{\mathcal{B}''\mathcal{B}}+\omega_{b''b}}\right\}$$

(c)

$$+\frac{1}{\hbar m}\sum_{B''b''}\sum_{\alpha\alpha'}^{N_M}{}'\left\{\frac{\langle B'|e^{-i\underline{k}_2\cdot\underline{R}_{\alpha'}}|B''\rangle\langle B''|e^{i\underline{k}_1\cdot\underline{R}_{\alpha}}|B\rangle\langle b'|\Pi_{\alpha'2}|b''\rangle\langle b''|\Pi_{\alpha1}|b\rangle}{\omega_1-\omega_{b''b}-\omega_{B''B}}\right.$$

$$\left.-\frac{\langle B'|e^{i\underline{k}_1\cdot\underline{R}_{\alpha}}|B''\rangle\langle B''|e^{-i\underline{k}_2\cdot\underline{R}_{\alpha'}}|B\rangle\langle b'|\Pi_{\alpha1}|b''\rangle\langle b''|\Pi_{\alpha'2}|b\rangle}{\omega_2+\omega_{b''b}+\omega_{B''B}}\right\}$$

(d)

$$+\frac{1}{\hbar m}\sum_{B''}\sum_{\alpha}^{N_M}\sum_{\gamma}^{N_e}\left\{\frac{\langle B'|e^{-i\underline{k}_2\cdot\underline{r}_\gamma}p_{\gamma2}|B''\rangle\langle B''|e^{i\underline{k}_1\cdot\underline{R}_{\alpha}}|B\rangle\langle b'|\Pi_{\alpha1}|b\rangle}{\omega_1-\omega_{b'b}-\omega_{B''B}}\right.$$

$$-\frac{\langle B'|e^{i\underline{k}_1\cdot\underline{r}_\gamma}p_{\gamma1}|B''\rangle\langle B''|e^{-i\underline{k}_2\cdot\underline{R}_{\alpha}}|B\rangle\langle b'|\Pi_{\alpha2}|b\rangle}{\omega_2+\omega_{b'b}+\omega_{B''B}}$$

$$+\frac{\langle B'|e^{-i\underline{k}_2\cdot\underline{R}_{\alpha}}|B''\rangle\langle B''|e^{i\underline{k}_1\cdot\underline{r}_\gamma}p_{\gamma1}|B\rangle\langle b'|\Pi_{\alpha2}|b\rangle}{\omega_1-\omega_{B''B}}$$

$$\left.-\frac{\langle B'|e^{i\underline{k}_1\cdot\underline{R}_{\alpha}}|B''\rangle\langle B''|e^{-i\underline{k}_2\cdot\underline{r}_\gamma}p_{\gamma2}|B\rangle\langle b'|\Pi_{\alpha1}|b\rangle}{\omega_2+\omega_{B''B}}\right\}$$

The various terms within the absolute square have been grouped into four sets. The first two sets, designated by (a) and (b), are included in Eq. (1.48). We wish to show here that sets (c) and (d) vanish in the ideal gas approximation and display a strong resonance behavior in a real gas. Consider the set of terms (c):

$$(c) = \frac{1}{\hbar m} \sum_{\mathcal{B}'' b''} \sum_{\alpha\beta}^{N_M}{}' \left\{ \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle \langle b' | \Pi_{\beta 2} | b'' \rangle \langle b'' | \Pi_{\alpha 1} | b \rangle}{\omega_1 - \omega_{b''b} - \omega_{\mathcal{B}''\mathcal{B}}} \right.$$

$$\left. - \frac{\langle \mathcal{B}' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B} \rangle \langle b' | \Pi_{\alpha 1} | b'' \rangle \langle b'' | \Pi_{\alpha 2} | b \rangle}{\omega_2 + \omega_{b''b} + \omega_{\mathcal{B}''\mathcal{B}}} \right\} \qquad (C.2)$$

Assuming that the Hamiltonian for the internal states is of the form

$$H^N = \sum_{\alpha}^{N_M} H_\alpha^N \qquad (C.3)$$

and that the particles are separately distinguishable, as in Chapter I, the internal state functions may be chosen to factor into individual particle internal state functions so that for example

$$|b\rangle = |b_1\rangle |b_2\rangle \cdots |b_\alpha\rangle \cdots |b_\beta\rangle \cdots |b_{N_M}\rangle \qquad (C.4)$$

It follows then that in the first term in (C.2)

$$\omega_{b''b} = \omega_{b'_\alpha b_\alpha}$$

and in the second term

$$\omega_{b''b} = \omega_{b'_\beta b_\beta}$$

In the ideal gas approximation

$$H^X = \sum_{\alpha}^{N_M} \frac{P_\alpha^2}{2M_\alpha} \qquad (C.5)$$

and consequently the external state functions may also be factored such that for example

$$|\mathcal{B}\rangle = |\mathcal{B}_1\rangle|\mathcal{B}_2\rangle\cdots|\mathcal{B}_\alpha\rangle\cdots|\mathcal{B}_\beta\rangle\cdots|\mathcal{B}_{N_M}\rangle \qquad (C.6)$$

It follows that Eq. (C.2) may be written in the form

$$(c) = \sum_{\alpha\beta}{}' \langle\mathcal{B}'_\beta|e^{-i\underline{k}_2\cdot\underline{R}_\beta}|\mathcal{B}_\beta\rangle\langle\mathcal{B}'_\alpha|e^{i\underline{k}_1\cdot\underline{R}_\alpha}|\mathcal{B}_\alpha\rangle \qquad (C.7)$$

$$(\times)\langle b'_\beta|\Pi_{\beta 2}|b_\beta\rangle\langle b'_\alpha|\Pi_{\alpha 1}|b_\alpha\rangle\left\{\frac{1}{\omega_1-\omega_{b'_\alpha b_\alpha}-\omega_{\mathcal{B}'_\alpha\mathcal{B}_\alpha}}-\frac{1}{\omega_2+\omega_{b'_\beta b_\beta}+\omega_{\mathcal{B}'_\beta\mathcal{B}_\beta}}\right\}$$

From the energy-conserving delta function in Eq. (C.1), for all non-vanishing contributions to $T_{\mathcal{B}b\eta\rightarrow\mathcal{B}'b'\eta'}$

$$\omega_1-\omega_{b'_\alpha b_\alpha}-\omega_{\mathcal{B}'_\alpha\mathcal{B}_\alpha}=\omega_2+\omega_{b'_\beta b_\beta}+\omega_{\mathcal{B}'_\beta\mathcal{B}_\beta}$$

in the ideal gas approximation. Substituting this result into Eq. (C.7) it is apparent that the set of terms (c) vanishes in the ideal gas approximation. The same result is obtained for the set of terms (d) and the free electron cross terms ($j\neq\ell$) in (b) in Eq. (C.1).

In a real gas, the external Hamiltonian H^X does not break up into a sum of single particle Hamiltonians and consequently the external state functions $|\mathcal{B}\rangle$ do not factor. In order to examine the terms (c) in Eq. (C.1) for this situation it is convenient to substitute $\omega_1+\omega_{b''b'}+\omega_{\mathcal{B}''\mathcal{B}'}$ for $\omega_2+\omega_{b''b}+\omega_{\mathcal{B}''\mathcal{B}}$ in the second term in Eq. (C.2).

This substitution is valid for all nonvanishing terms in Eq. (C.1) because of the energy-conserving δ-function. As a result one obtains

$$(C) = \frac{1}{\hbar m} \sum_{\mathcal{B}'' b''} {\sum_{\alpha\beta}}' \left\{ \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle \langle b' | \Pi_{\beta 2} | b'' \rangle \langle b'' | \Pi_{\alpha 1} | b \rangle}{\omega_1 - \omega_{b''b} - \omega_{\mathcal{B}''\mathcal{B}}} \right.$$

$$\left. - \frac{\langle \mathcal{B}' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B} \rangle \langle b' | \Pi_{\alpha 1} | b'' \rangle \langle b'' | \Pi_{\beta 2} | b \rangle}{\omega_1 + \omega_{b''b'} + \omega_{\mathcal{B}''\mathcal{B}'}} \right\}$$

Noting that the <u>internal</u> state functions still factor, Eq. (C.8) becomes

(C.9)

$$(C) = \frac{1}{\hbar m} {\sum_{\alpha\beta}}' \langle b'_\beta | \Pi_{\beta 2} | b_\beta \rangle \langle b'_\alpha | \Pi_{\alpha 1} | b_\alpha \rangle$$

$$(\times) \sum_{\mathcal{B}''} \left\{ \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_1 - \omega_{b'_\alpha b_\alpha} - \omega_{\mathcal{B}''\mathcal{B}}} \right.$$

$$\left. - \frac{\langle \mathcal{B}' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B} \rangle}{\omega_1 - \omega_{b'_\alpha b_\alpha} + \omega_{\mathcal{B}''\mathcal{B}'}} \right\}$$

At this point it is convenient to introduce the expansions

$$\frac{1}{\omega_1 - \omega_{b'_\alpha b_\alpha} - \omega_{\mathcal{B}''\mathcal{B}}} = \frac{1}{\omega_1 - \omega_{b'_\alpha b_\alpha}} \sum_{n=0}^{\infty} \left(\frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_1 - \omega_{b'_\alpha b_\alpha}} \right)^n$$

(C.10)

$$\frac{1}{\omega_1 - \omega_{b'_\alpha b_\alpha} - \omega_{\mathcal{B}''\mathcal{B}}} = \frac{1}{\omega_1 - \omega_{b'_\alpha b_\alpha}} \sum_{n=0}^{\infty} \left(\frac{\omega_{\mathcal{B}'\mathcal{B}''}}{\omega_1 - \omega_{b'_\alpha b_\alpha}} \right)^n$$

which converge, of course, only for $|\omega_{\mathcal{B}''\mathcal{B}}|$ and $|\omega_{\mathcal{B}'\mathcal{B}''}|$ less than $\omega_1 - \omega_{b'_\alpha b_\alpha}$. Restricting present consideration to separations from resonance which are sufficient to satisfy this requirement for all significant matrix elements in the sum over $\mathcal{B}''$ in Eq. (C.9), one obtains

$$(C) = \frac{1}{\hbar m} \sum_{\alpha\beta} \frac{\langle b'_\beta | \Pi_{\beta 2} | b_\beta \rangle \langle b'_\alpha | \Pi_{\alpha 1} | b_\alpha \rangle}{\omega_1 - \omega_{b'_\alpha b_\alpha}}$$

$$(\times) \sum_{\mathcal{B}''} \sum_{n=0}^{\infty} \left\{ \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | [H^X, e^{i\underline{k}_1 \cdot \underline{R}_\alpha}]^n | \mathcal{B} \rangle}{(\omega_1 - \omega_{b'_\alpha b_\alpha})^n \hbar^n} \right. \tag{C.11}$$

$$\left. - \frac{\langle \mathcal{B}' | [H^X, e^{i\underline{k}_1 \cdot \underline{R}_\alpha}]^n | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\beta} | \mathcal{B} \rangle}{(\omega_1 - \omega_{b'_\alpha b_\alpha})^n \hbar^n} \right\}$$

Summing over intermediate external states, Eq. (C.11) becomes

$$(C) = \frac{1}{\hbar m} \sum_{\alpha\beta} \frac{\langle b'_\beta | \Pi_{\beta 2} | b_\beta \rangle \langle b'_\alpha | \Pi_{\alpha 1} | b_\alpha \rangle}{\omega_1 - \omega_{b'_\alpha b_\alpha}}$$

$$(\times) \sum_{n} \frac{\langle \mathcal{B}' | [e^{-i\underline{k}_2 \cdot \underline{R}_\beta}, [H^X, e^{i\underline{k}_1 \cdot \underline{R}_\alpha}]^n] | \mathcal{B} \rangle}{(\omega_1 - \omega_{b'_\alpha b_\alpha})^n \hbar^n} \tag{C.12}$$

The Hamiltonian H^X introduced in Section 1.1 is of the form

$$H^X = \sum_{\alpha}^{N} \frac{P_\alpha^2}{2M_\alpha} + H^I$$

where the sum over α runs over all particles (including any free electrons). Assuming that H^I commutes with $\underline{R}_\alpha$ for all α, the first non-vanishing term in the sum over n occurs for n = 3, and one obtains for this term

$$(C) \cong \frac{1}{m} \sum_{\alpha\beta} \frac{\langle b'_\beta | \Pi_{\beta 2} | b_\beta \rangle \langle b'_\alpha | \Pi_{\alpha 1} | b_\alpha \rangle}{\hbar^4 (\omega_1 - \omega_{b'_\alpha b_\alpha})^4} \tag{C.13}$$

$$\langle \mathcal{B}' | [e^{-i \underline{k}_2 \cdot \underline{R}_\beta}, [H^x, e^{i \underline{k}_1 \cdot \underline{R}_\alpha}]^3] | \mathcal{B} \rangle$$

Thus the first nonvanishing term has a strong resonance behavior. A quantitative estimate of the significance of this term has not been worked out here. However, the strong resonance behavior suggests that it should not be significant in a real gas away from resonance, if significant at all. The same argument can be advanced for the terms (d) in Eq. (C.1).

APPENDIX D

ON THE SUM OVER INTERMEDIATE EXTERNAL STATES

In this appendix the approximation introduced in Section 2.2 to facilitate the sum over intermediate external states is evaluated in the ideal gas approximation.

Consider the first of the second-order terms in Eq. (2.1). This term involves

$$\sum_{\mathcal{B}''} \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_1 - \omega_{\mathcal{B}''\mathcal{B}} - \omega_{b''b}} \tag{D.1}$$

It is convenient to introduce the expansion

$$\frac{1}{\omega_1 - \omega_{\mathcal{B}''\mathcal{B}} - \omega_{b''b}} = \frac{1}{\omega_1 - \omega_{b''b}} \sum_{n=0}^{\infty} \left(\frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_1 - \omega_{b''b}} \right)^n \tag{D.2}$$

which converges for

$$|\omega_{\mathcal{B}''\mathcal{B}}| < \omega_1 - \omega_{b''b} \tag{D.3}$$

Restricting consideration to separations from the resonance which are sufficiently large so that this condition is satisfied for all significant matrix elements $\langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle$, we may substitute Eq. (D.2) into (D.1) to obtain

$$\sum_{\mathcal{B}''} \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_1 - \omega_{\mathcal{B}''\mathcal{B}} - \omega_{b''b}} \tag{D.4}$$

$$= \sum_{\mathcal{B}''} \frac{\langle \mathcal{B}' | e^{-i\underline{k}_2 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_1 - \omega_{b''b}} \left[1 + \left(\frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_1 - \omega_{b''b}} \right) + \cdots \right]$$

In the ideal gas approximation the Hamiltonian H^x becomes

$$H^x = \sum_{\alpha}^{N} H^x_\alpha = \sum_{\alpha}^{N} \frac{P_\alpha^2}{2M_\alpha} \tag{D.5}$$

Consequently, the external state functions may be written in the form

$$|\mathcal{B}\rangle = |\mathcal{B}_1\rangle |\mathcal{B}_2\rangle \cdots |\mathcal{B}_\alpha\rangle \cdots |\mathcal{B}_N\rangle \tag{D.6}$$

where

$$|\mathcal{B}_\alpha\rangle = \frac{1}{L^3} e^{i\underline{k}_\alpha \cdot \underline{R}_\alpha} \tag{D.7}$$

Here we have utilized box normalization.[53] The energy of the particle α associated with the state $|\mathcal{B}_\alpha\rangle$ is given by

$$H^x_\alpha |\mathcal{B}_\alpha\rangle = \frac{P_\alpha^2}{2M_\alpha} |\mathcal{B}_\alpha\rangle = \frac{\hbar^2 k_\alpha^2}{2M_\alpha} \tag{D.8}$$

In the ideal gas the energy difference $\hbar\omega_{\mathcal{B}''\mathcal{B}}$ between initial and intermediate external states is determined by the matrix element

$$\langle \mathcal{B}'' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle \tag{D.9}$$

and the initial state $|\mathcal{B}>$. Thus we find

$$\omega_{\mathcal{B}''\mathcal{B}} = \underline{v}_\alpha \cdot \underline{k}_1 + \frac{\hbar k_1^2}{2M_\alpha} \tag{D.10}$$

The second term is usually very much smaller that the first. Neglecting it for simplicity, one obtains

$$\frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_1 - \omega_{b''b}} = \frac{\underline{v}_\alpha \cdot \underline{k}_1}{\omega_1 - \omega_{b''b}} \tag{D.11}$$

A similar result obtains for the second of the second order terms in Eq. (2.1). For this term it is convenient to introduce the expansion

$$\sum_{\mathcal{B}''} \frac{\langle \mathcal{B}' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_2 + \omega_{b''b} + \omega_{\mathcal{B}''\mathcal{B}}} \tag{D.12}$$

$$= \sum_{\mathcal{B}''} \frac{\langle \mathcal{B}' | e^{i\underline{k}_1 \cdot \underline{R}_\alpha} | \mathcal{B}'' \rangle \langle \mathcal{B}'' | e^{-i\underline{k}_2 \cdot \underline{R}_\alpha} | \mathcal{B} \rangle}{\omega_2 + \omega_{b''b}} \left[1 - \frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_2 + \omega_{b''b}} + \cdots \right]$$

One finds

$$\frac{\omega_{\mathcal{B}''\mathcal{B}}}{\omega_2 + \omega_{b''b}} = \frac{-\underline{v}_\alpha \cdot \underline{k}_2}{\omega_2 + \omega_{b''b}}$$

The expression $\underline{v}_\alpha \cdot \underline{k}_1$ in Eq. (D.11) gives the Doppler shift in frequency (to first order) associated with the emission of a photon in direction $-\underline{k}_1$ with frequency ck_1 by a particle with velocity $\underline{v}_\alpha$. It follows that $(\underline{v}_\alpha \cdot \underline{k}_1)/(\omega_1 - \omega_{b''b})$ will be small for all particle velocities of significant probability if the separation from resonance

$\omega_1-\omega_{b''b}$ is large compared with the Doppler broadening (and shift, if any) associated with emission lines in the scattering system. The same conclusion holds for the term $(-\underline{v}_\alpha\cdot\underline{k}_2)/(\omega_2+\omega_{b''b})$. In this case, it appears that in the ideal gas approximation the expansions in Eqs. (D.4) and (D.12) are dominated by the first terms and one may ignore $\omega_{\mathcal{B}''\mathcal{B}}$ to a good approximation.

As pointed out in Section 4.1, the first-order and second-order terms in the scattering cross section often are of nearly the same magnitude and opposite sign, so that the cross section is associated with the small difference between two large quantities. In such a case approximation of the type discussed in this appendix must, of course, be introduced with care, for a small error in the second-order term may lead to a large error in the cross section. However, for light scattering the difference in absolute magnitudes of first- and second-order terms is usually about 10% of one term or greater* and at least in such a case this problem does not appear to be serious.

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*See Section 4.1.

APPENDIX E

VAN HOVE G-FUNCTIONS AND THEIR CLASSICAL LIMITS IN THE IDEAL GAS APPROXIMATION

In this appendix the Van Hove G-functions are calculated in the ideal gas approximation and the resulting cross sections are compared to those obtained using the classical limits of these functions obtained through the Vineyard perscription.

From Eqs. (2.29), (2.27) and (2.28)

$$G(\underline{\rho},\tau) = G^{S}(\underline{\rho},\tau) + G^{P}(\underline{\rho},\tau) \tag{E.1}$$

$$G^{S}(\underline{\rho},\tau) = \sum_{\alpha} G_{\alpha\alpha}(\underline{\rho},\tau) \tag{E.2}$$

$$G(\underline{\rho},\tau) = \sum_{\alpha\alpha'}{}' G_{\alpha\alpha'}(\underline{\rho},\tau) \tag{E.3}$$

From Eqs. (2.13) and (2.7)

$$\begin{aligned} G_{\alpha\alpha'}(\underline{\rho},\tau) = {} & (2\pi)^{-3} N^{-1} \int d^3\kappa \, e^{i\underline{\kappa}\cdot\underline{\rho}} \\ & (\times) \left\langle e^{-i\underline{\kappa}\cdot\underline{R}_\alpha} e^{\frac{i\tau}{\hbar}H^x} e^{i\underline{\kappa}\cdot\underline{R}_\alpha} e^{-\frac{i\tau}{\hbar}H^x} \right\rangle \\ & (2\pi)^{-3} N^{-1} \int d^3\kappa \, e^{i\underline{\kappa}\cdot\underline{\rho}} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i\tau}{\hbar}\right)^n \left\langle e^{-i\underline{\kappa}\cdot\underline{R}_\alpha} \left[H^x, e^{i\underline{\kappa}\cdot\underline{R}_{\alpha'}}\right]^n \right\rangle \end{aligned} \tag{E.4}$$

In the ideal gas approximation

$$H^x = \sum_{\alpha} \frac{P_\alpha^2}{2M_\alpha} \tag{E.5}$$

and

$$\left[H^{\times}, e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\right]^{n} = e^{i\underline{k}\cdot\underline{R}_{\alpha'}}\left(\frac{\hbar}{M_\alpha}\underline{k}\cdot\underline{P}_\alpha + \frac{\hbar^2 k^2}{2M_\alpha}\right)^{n} \tag{E.6}$$

Then

$$G_{\alpha\alpha'}(\underline{\rho},\tau) = (2\pi)^{-3}N^{-1}\int d^3k\, e^{i\underline{k}\cdot\underline{\rho}} \tag{E.7}$$

$$(\times)\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i\tau}{\hbar}\right)^{n}\left\langle e^{i\underline{k}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{k}\cdot\underline{P}_\alpha + \frac{\hbar^2k^2}{2M_\alpha}\right)^{n}\right\rangle$$

Consider

$$\left\langle e^{i\underline{k}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{k}\cdot\underline{P}_\alpha + \frac{\hbar^2k^2}{2M_\alpha}\right)^{n}\right\rangle$$

$$= \sum_{\mathcal{B}} P_{\mathcal{B}}\left\langle \mathcal{B}\right| e^{i\underline{k}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{k}\cdot\underline{P}_\alpha + \frac{\hbar^2k^2}{2M_\alpha}\right)^{n}\left|\mathcal{B}\right\rangle \tag{E.8}$$

As noted previously, in the ideal gas approximation the external state functions may be chosen to factor as follows

$$|\mathcal{B}\rangle = |\mathcal{B}_1\rangle|\mathcal{B}_2\rangle\cdots|\mathcal{B}_\alpha\rangle\cdots|\mathcal{B}_{\alpha'}\rangle\cdots|\mathcal{B}_N\rangle \tag{E.9}$$

where, for example, the individual particle state functions may be chosen to take the form

$$|\mathcal{B}_\alpha\rangle = \frac{1}{L^{3/2}}e^{i\underline{k}_\alpha\cdot\underline{R}_\alpha} \tag{E.10}$$

Here box normalization[53] has been employed. Substituting from Eqs. (E.9) and (E.10) into Eq. (E.8) one obtains for $\alpha \neq \alpha'$

$$\left\langle e^{i\underline{\kappa}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{\kappa}\cdot\underline{P}_\alpha+\frac{\hbar^2\kappa^2}{2M_\alpha}\right)^n\right\rangle \tag{E.11}$$

$$=\frac{1}{L^6}\sum_{k_\alpha k_{\alpha'}}P_{k_\alpha}P_{k_{\alpha'}}\int d^3R_\alpha d^3R_{\alpha'}\,e^{i\underline{\kappa}\cdot(R_{\alpha'}-R_{\alpha})}\left(\frac{\hbar^2}{M_\alpha}\underline{\kappa}\cdot\underline{k}+\frac{\hbar^2\kappa^2}{2M_\alpha}\right)^n$$

In the limit as L → ∞, the sums over $\underline{k}_\alpha$ and $\underline{k}_{\alpha'}$ may be replaced by integrals; i.e.,

$$\sum_{k_\alpha}P_{k_\alpha}\longrightarrow\int d^3k_\alpha\,P(\underline{k}_\alpha) \tag{E.12}$$

Then Eq. (E.11) becomes

$$\left\langle e^{i\underline{\kappa}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{\kappa}\cdot\underline{P}_\alpha+\frac{\hbar^2\kappa^2}{2M_\alpha}\right)^2\right\rangle$$

$$=\frac{1}{L^6}\int d^3k_\alpha d^3k_{\alpha'}P(\underline{k}_\alpha)P(\underline{k}_{\alpha'})\int d^3R_\alpha d^3R_{\alpha'} \tag{E.13}$$

$$(\mathrm{x})\;e^{i\underline{\kappa}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar^2}{M_\alpha}\underline{\kappa}\cdot\underline{k}_\alpha+\frac{\hbar^2}{2M_\alpha}\kappa^2\right)^n$$

The integrals over R_α and $R_{\alpha'}$ may be carried out directly, yielding $(2\pi L)^3\delta(\kappa)\delta_{n,o}$. Thus one obtains for $\alpha \neq \alpha'$

$$\left\langle e^{i\underline{\kappa}\cdot(\underline{R}_{\alpha'}-\underline{R}_\alpha)}\left(\frac{\hbar}{M_\alpha}\underline{\kappa}\cdot\underline{P}_\alpha+\frac{\hbar^2\kappa^2}{2M_\alpha}\right)^n\right\rangle=\left(\frac{2\pi}{L}\right)^3\delta(\underline{\kappa})\,\delta_{n,o} \tag{E.14}$$

Substituting this result into Eq. (E.7), one obtains

$$G_{\alpha\alpha'}(f,\tau)=\frac{1}{NL^3} \tag{E.15}$$

for $\alpha \neq \alpha'$. Finally, substituting this result into Eq. (E.3),

$$G^{P}_{IG}(\rho,\tau) = \frac{N-1}{L^3} \cong N_0 \tag{E.16}$$

where N_0 is the particle density.

The subscript IG is inserted to designate that this result is obtained in the ideal gas approximation.

Now consider $G_{\alpha\alpha}(\rho_-,\tau)$. From Eq. (E.7)

$$\begin{aligned} G_{\alpha\alpha}(\rho,\tau) &= \int d^3\kappa\, e^{i\underline{\kappa}\cdot\underline{\rho}} \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{i\tau}{\hbar}\right)^n \left\langle \left(\frac{\hbar^2}{M_\alpha}\underline{\kappa}\cdot\underline{k}_\alpha + \frac{\hbar^2\kappa^2}{2M_\alpha}\right)^n \right\rangle \\ & \int d^3\kappa\, e^{i\underline{\kappa}\cdot\underline{\rho}} \left\langle e^{\frac{i\hbar\tau}{M_\alpha}(\underline{\kappa}\cdot\underline{k}_\alpha + \kappa^2/2)} \right\rangle \end{aligned} \tag{E.17}$$

For the average over external states one obtains

$$\left\langle e^{\frac{i\hbar\tau}{M_\alpha}(\underline{\kappa}\cdot\underline{k}_\alpha + \kappa^2/2)} \right\rangle = \int d^3k_\alpha P(\underline{k}_\alpha)\, e^{\frac{i\hbar\tau}{M_\alpha}(\underline{\kappa}\cdot\underline{k}_\alpha + \kappa^2/2)} \tag{E.18}$$

Assuming a system of like particles in a Maxwellian velocity distribution at a temperature Θ

$$P(\underline{k}_\alpha) = \left(\frac{\hbar^2}{2\pi M\Theta}\right)^{3/2} e^{-\frac{\hbar^2 k_\alpha^2}{2M\Theta}} \tag{E.19}$$

Substituting this distribution into Eq. (E.18), the integral over $\underline{k}_\alpha$ may be performed directly, yielding

$$\left\langle e^{\frac{i\hbar\tau}{M}(\underline{\kappa}\cdot\underline{k}_\alpha + \kappa^2/2} \right\rangle = e^{-\frac{\xi\tau^2}{2M}\kappa^2} \tag{E.20}$$

where

$$\xi = \Theta - \frac{i\hbar}{\tau} \tag{E.21}$$

Substituting Eq. (E.20) into (E.17) and integrating over $\underline{\kappa}$ one obtains

$$G_{\alpha\alpha}(\underline{\rho},\tau) = \frac{1}{N}\left(\frac{M}{2\pi\tau^2\xi}\right)^{3/2} e^{-\frac{M\rho^2\kappa^2}{2\tau^2\xi}} \tag{E.22}$$

Then from Eq. (E.2)

$$G^S(\underline{\rho},\tau) = \left(\frac{M}{2\pi\tau^2\xi}\right)^{3/2} e^{-\frac{M\rho^2\kappa^2}{2\tau^2\xi}} \tag{E.23}$$

The cross sections developed in Section 2.1 are proportional to $S^S(\underline{\kappa},\omega)$, $S^P(\underline{\kappa},\omega)$ or $S(\underline{\kappa},\omega)$ where for example

$$S(\underline{\kappa},\omega) = \frac{1}{2\pi}\int d^3\rho\, d\tau\, e^{i[\underline{\kappa}\cdot\underline{\rho}-\omega\tau]}\, G(\underline{\rho},\tau) \tag{E.24}$$

Substituting from Eq. (E.16) for $G^P(\underline{\rho},\tau)$, one obtains for $S^P(\underline{\kappa},\omega)$ in the ideal gas approximation

$$S^P_{IG}(\underline{\kappa},\omega) = (2\pi)^2\,\frac{N-1}{L^3}\,\delta(\underline{\kappa})\,\delta(\omega) \tag{E.25}$$

Likewise, substituting from Eq. (E.23) for $G^S(\underline{\rho},\tau)$, one obtains for $S^S(\underline{\kappa},\omega)$ in the ideal gas approximation

$$S^S_{IG}(\underline{\kappa},\omega) = \frac{1}{2\pi}\int d^3\rho\, d\tau\, e^{i[\underline{\kappa}\cdot\underline{\rho}-\omega\tau]}\left(\frac{M}{2\pi\tau^2\xi}\right)^{3/2} e^{-\frac{M\rho^2}{2\tau^2\xi}} \tag{E.26}$$

The integrations over $\underline{\rho}$ and τ may be performed directly, yielding

$$S^S_{IG}(\underline{\kappa},\omega) = \left(\frac{M}{2\pi\Theta\kappa^2}\right)^{1/2} e^{-\frac{M}{2\Theta\kappa^2}\left(\omega-\frac{\hbar\kappa^2}{2M}\right)^2} \tag{E.27}$$

Now consider the classical limits for $G^P(\rho_-,\tau)$ and $G^S(\rho_-,\tau)$ obtained through the Vineyard perscription.* Using, for example, the method of Lamb[38] to evaluate the classical average

$$\left\langle \delta\left[\underline{R}_\alpha(0)+\underline{\rho}-\underline{R}_{\alpha'}(\tau)\right]\right\rangle$$

one obtains from Eq. (2.36)

$$\mathcal{G}^P_{IG}(\underline{\rho},\tau) = \frac{N-1}{L^3} \tag{E.28}$$

$$\mathcal{G}^S_{IG}(\underline{\rho},\tau) = \left(\frac{M}{2\pi\tau^2\Theta}\right)^{3/2} e^{-\frac{M\rho^2}{2\tau^2\Theta}} \tag{E.29}$$

Thus $\mathcal{G}^S_{IG}(\rho_-,\tau)$ is identical to $G^S_{IG}(\rho_-,\tau)$. On the other hand, $\mathcal{G}^P_{IG}(\rho_-,\tau)$ differs from $G^P_{IG}(\underline{\rho},\tau)$ in that $\xi = \Theta - i\hbar/\tau$ is replaced by just Θ.

Substituting from Eqs. (E.28) and (E.29) into Eq. (E.24) for $G(\underline{\rho},\tau)$, one obtains in the classical limit

$$\mathcal{S}^P_{IG}(\underline{\kappa},\omega) = (2\pi)^2\frac{N-1}{L^3}\delta(\underline{\kappa})\delta(\omega) \tag{E.30}$$

and

$$\mathcal{S}^S_{IG}(\underline{\kappa},\omega) = \left(\frac{M}{2\pi\Theta\kappa^2}\right)^{1/2} e^{-\frac{M\omega^2}{2\Theta\kappa^2}} \tag{E.31}$$

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*See the discussion following Eq. (2.35) for a description of the Vineyard perscription.

As expected, $\mathcal{S}^{P}_{IG}(\underline{\kappa},\omega)$ is identical to its quantum counterpart $S^{P}_{IG}(\underline{\kappa},\omega)$. However, $\mathcal{S}^{S}_{IG}(\underline{\kappa},\omega)$ differs from $S^{S}_{IG}(\underline{\kappa},\omega)$ in that $(\omega - \hbar\kappa^{2}/2M)$ in the latter is replaced by ω in the former. The extra term $\hbar\kappa^{2}/2M$ in the quantum result arises from the term $i\hbar/\tau$ in $G^{S}_{IG}(\underline{\rho},\tau)$ which is not present in $\mathcal{G}^{S}_{IG}(\underline{\rho},\tau)$. Neglecting the small variation in κ^{2} as ω ranges over a typically sharp line, the term $\hbar\kappa^{2}/2M$ contributes a constant frequency shift which is omitted in the classical limit. For light scattering from atoms this shift is on the order of 10^{7} $\sec^{-1}$, whereas for scattering from free electrons it is on the order of 10^{10} $\sec^{-1}$. Comparing these shifts to typical Doppler broadening line widths, on the order of 10^{10} $\sec^{-1}$ for atoms at 300 °K and 10^{12} $\sec^{-1}$ for free electrons at 10,000 °K, it is evident that in the ideal gas approximation the shifts neglected in the Vineyard perscription classical limits are very small and probably insignificant for most purposes.

APPENDIX F

THE RELATIONSHIP BETWEEN $(Q_0^1)_{\tau J\to\tau J}$ AND $(Q_1^1)_{\tau J\to\tau J}$

From Eqs. (4.76), (4.70) and (4.69)

$$(Q_0^1)_{\tau J\to\tau J} = \frac{4}{\hbar^2(2J+1)}\sum_M \left|\sum_{\tau''J''}\frac{\omega_{\tau''J'',\tau J}}{\omega^2_{\tau''J'',\tau J}-\omega_1^2}\right. \tag{F.1}$$

$$(x)\ \left.|\langle\tau J\|D\|\tau''J''\rangle|^2\left\{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}^2-\frac{1}{3(2J+1)}\right\}\right|^2$$

From Eqs. (4.77) and (4.70)

$$(Q_1^1)_{\tau J\to\tau J} = \frac{1}{\hbar^2(2J+1)}\sum_M \left|\sum_{\tau''J''}|\langle\tau J\|D\|\tau''J''\rangle|^2\right. \tag{F.2}$$

$$(x)\left\{\frac{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & -1 & M\end{pmatrix}}{\omega_{\tau''J'',\tau J}-\omega_1}-\frac{\begin{pmatrix} J & 1 & J'' \\ -M & 1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & 0 & M'\end{pmatrix}}{\omega_{\tau''J'',\tau J}+\omega_1}\right\}$$

Multiplying out the first absolute square in Eq. (F.1), one obtains

$$(Q_0^1)_{\tau J\to\tau J} = \frac{4}{\hbar^2(2J+1)}\sum_M\sum_{\tau''J''}\sum_{\tau'''J'''}\frac{\omega_{\tau''J'',\tau J}\,\omega_{\tau'''J''',\tau J}}{(\omega^2_{\tau''J'',\tau J}-\omega_1^2)(\omega^2_{\tau'''J''',\tau J}-\omega_1^2)}$$

$$(x)\ |\langle\tau J\|D\|\tau''J''\rangle|^2\,|\langle\tau J\|D\|\tau'''J'''\rangle|^2 \tag{F.3}$$

$$(x)\left\{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}^2\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M\end{pmatrix}^2-\left[\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}^2+\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M\end{pmatrix}^2\right]\frac{1}{3(2J+1)}+\frac{1}{9(2J+1)^2}\right\}$$

Summing over M employing an orthogonality property of the 3-J symbols, one obtains

$$(Q_0^1)_{\tau J \to \tau J} = \frac{4}{\hbar^2(2J+1)} \sum_{\tau'' J''} \sum_{\tau''' J'''} \frac{\omega_{\tau'' J'', \tau J}\, \omega_{\tau''' J''', \tau J}}{(\omega^2_{\tau'' J'', \tau J} - \omega_1^2)(\omega^2_{\tau''' J''', \tau J} - \omega_1^2)}$$

$$(X)\ \left|\langle \tau J \| D \| \tau'' J'' \rangle\right|^2 \left|\langle \tau J \| D \| \tau''' J''' \rangle\right|^2 \tag{F.4}$$

$$(X)\left\{\sum_M \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix}^2 - \frac{1}{9(2J+1)}\right\}$$

Consider $\sum_M \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix}^2$. It is convenient to express the 3-J symbols in terms of Clebsch-Gordan coefficients in order to obtain notation similar to that of Ref. 77 . Thus

$$\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix} = \begin{pmatrix} J'' & 1 & J \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix}$$

$$= \frac{(-1)^{J''-J}}{\sqrt{(2J+1)(2J'''+1)}}\, C^{J'' 1 J}_{-M 0}\, C^{J 1 J'''}_{-M 0} \tag{F.5}$$

Employing a general relationship between Clebsch-Gordan coefficients and Racah coefficients,[77] one obtains

$$C^{J'' 1 J}_{-M 0}\, C^{J 1 J'''}_{-M 0} = \sqrt{2J+1} \sum_S \sqrt{2S+1}\, C^{11S}_{00}\, C^{J'' S J'''}_{-M 0}\, W(J'' 1 J''' 1; JS) \tag{F.6}$$

where W(abcd;ef) is a Racah coefficient. Substituting this result into Eq. (F.5), one obtains

$$\sum_{M} \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix}^2 = \frac{1}{2J'''+1} \sum_{SS'} W(J''1J'''1;JS) \tag{F.7}$$

$$(\times)\; W(J''1J'''1;JS')\, C^{11S}_{00}\, C^{11S'}_{00} \sum_{M} C^{J''SJ'''}_{-M0}\, C^{J''S'J'''}_{-M0}$$

Consider

$$\sum_{M} C^{J''SJ'''}_{-M0}\, C^{J''S'J'''}_{-M0} = \frac{2J'''+1}{\sqrt{(2S+1)(2S'+1)}} \sum_{M} C^{J''J'''S}_{-MM}\, C^{J''J'''S'}_{-MM} \tag{F.8}$$

$$= \frac{2J'''+1}{2S+1}\, \delta_{SS'}$$

The last step is a result of an orthogonality property of the Clebsch-Gordan coefficients.[54] Substituting this result into Eq. (F.7), one obtains

$$\sum_{M} \begin{pmatrix} J & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \begin{pmatrix} J & 1 & J''' \\ -M & 0 & M \end{pmatrix}^2 = \sum_{S} W^2(J''1J'''1;JS) \left(C^{11S}_{00}\right)^2 \tag{F.9}$$

From the orthogonality property of Racah coefficients[77]

$$\frac{1}{9} \sum_{S} (2S+1)\, W^2(J''1J'''1;JS) = \frac{1}{9(2J+1)} \tag{F.10}$$

Finally, substituting from Eqs. (F.9) and (F.10) into Eq. (F.4), one obtains

$$\left(Q^{1}_{0}\right)_{\tau J \to \tau J} = \frac{4}{\hbar^2 (2J+1)} \sum_{\substack{\tau'' J'' \\ \tau''' J'''}} \frac{\omega_{\tau''J'',\tau J}\;\; \omega_{\tau'''J''',\tau J}}{\left(\omega^2_{\tau''J'',\tau J} - \omega_1^2\right)\left(\omega^2_{\tau'''J''',\tau J} - \omega_1^2\right)} \tag{F.11}$$

$$(\times)\; \left|\langle \tau J \| D \| \tau'' J'' \rangle\right|^2 \left|\langle \tau J \| D \| \tau''' J''' \rangle\right|^2$$

$$(\times) \sum_{S} W^2(J''1J'''1;JS) \left\{ \left(C^{11S}_{00}\right)^2 - \frac{2S+1}{9} \right\}$$

Now consider $(Q_1^1)_{\tau J \to \tau J}$. Writing out the first absolute square in Eq. (F.2) one obtains

$$
\begin{aligned}
(Q_1^1)_{\tau J\to\tau J} = \frac{1}{\hbar^2(2J+1)} \sum_{\substack{\tau'' J''\\ \tau''' J'''}} \left|\langle \tau J \| D \| \tau'' J''\rangle\right|^2 \left|\langle \tau J \| D \| \tau''' J'''\rangle\right|^2 \\
(\times) \sum_{MM'} \Bigg\{ \frac{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & -1 & M\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M' & -1 & M\end{pmatrix}}{(\omega_{\tau''J'',\tau J}-\omega_1)(\omega_{\tau'''J''',\tau J}-\omega_1)} \qquad \text{(F.12)} \\
- \frac{\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & -1 & M\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M' & 0 & M'\end{pmatrix}}{(\omega_{\tau''J'',\tau J}-\omega_1)(\omega_{\tau''J'',\tau J}+\omega_1)} \\
- \frac{\begin{pmatrix} J & 1 & J'' \\ -M & 1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & 0 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 0 & M\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M' & -1 & M\end{pmatrix}}{(\omega_{\tau''J'',\tau J}+\omega_1)(\omega_{\tau'''J''',\tau J}-\omega_1)} \\
+ \frac{\begin{pmatrix} J & 1 & J'' \\ -M & 1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M' & 0 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M & 1 & M'\end{pmatrix}\begin{pmatrix} J & 1 & J''' \\ -M' & 0 & M'\end{pmatrix}}{(\omega_{\tau''J'',\tau J}+\omega_1)(\omega_{\tau'''J''',\tau J}+\omega_1)} \Bigg\}
\end{aligned}
$$

Employing the same procedure used to reduce

$$
\begin{pmatrix} J & 1 & J'' \\ -M & 0 & M\end{pmatrix}^2 \begin{pmatrix} J & 1 & J''' \\ -M & 0 & M\end{pmatrix}^2
$$

in Eq. (F.9), the products of four 3-J symbols in Eq. (F.11) can be expressed in terms of Racah coefficients such that one obtains finally

$$(Q_1^1)_{\tau J\rightarrow\tau J}=\frac{2}{\hbar^2(2J+1)}\sum_{\substack{\tau''J''\\ \tau'''J'''}}\frac{|\langle\tau J\|D\|\tau''J''\rangle|^2\,|\langle\tau J\|D\|\tau'''J'''\rangle|^2}{(\omega^2_{\tau''J'',\tau J}-\omega_1^2)(\omega^2_{\tau'''J''',\tau J}-\omega_1^2)} \tag{F.13}$$

$$(X)\sum_S W^2(J''1J'''1;JS)$$

$$(X)\left\{\omega_{\tau''J'',\tau J}\,\omega_{\tau'''J''',\tau J}\left[C^{11S}_{01}C^{11S}_{10}-C^{11S}_{00}C^{11S}_{1-1}\right]\right.$$

$$\left.-\,\omega_1^2\left[C^{11S}_{01}C^{11S}_{10}+C^{11S}_{00}C^{11S}_{1-1}\right]\right\}.$$

The sums over S in Eqs. (F.11) and (F.13) range from S=0 to S=2. These two equations involve the quantities in Table F.1.

TABLE F.1

QUANTITIES INVOLVED IN EQS. (F.11) AND (F.13)

S	1	2	3
$\left[(C^{11S}_{00})^2-\frac{2S+1}{9}\right]$	$\frac{2}{9}$	$-\frac{1}{3}$	$\frac{1}{9}$
$\left[C^{11S}_{01}C^{11S}_{10}-C^{11S}_{00}C^{11S}_{1-1}\right]$	$\frac{1}{3}$	$-\frac{1}{2}$	$\frac{1}{6}$
$\left[C^{11S}_{01}C^{11S}_{10}+C^{11S}_{00}C^{11S}_{1-1}\right]$	$-\frac{1}{3}$	$-\frac{1}{2}$	$\frac{5}{6}$

From the table it is evident that

$$\left[C^{11S}_{01}C^{11S}_{10}-C^{11S}_{00}C^{11S}_{1-1}\right]=\frac{3}{2}\left[(C^{11S}_{00})^2-\frac{2S+1}{9}\right] \tag{F.14}$$

for all values of S of interest. Substituting this result into Eq. (F.13) and comparing with Eq. (F.11), one obtains

$$(Q_0^1)_{\tau J \to \tau J} = \frac{4}{3}\,(Q_1^1)_{\tau J \to \tau J} + \omega_1^2 F_{\tau J} \tag{F.15}$$

where

$$F_{\tau J} = \frac{2}{\hbar^2(2J+1)} \sum_{\substack{\tau'' J'' \\ \tau''' J'''}} \frac{\left|\langle \tau J \| D \| \tau'' J'' \rangle\right|^2 \left|\langle \tau J \| D \| \tau''' J''' \rangle\right|^2}{(\omega^2_{\tau'' J'', \tau J} - \omega_1^2)(\omega^2_{\tau''' J''', \tau J} - \omega_1^2)} \tag{F.16}$$

$$(\mathrm{x}) \sum_{S} W^2(J''1\,J'''1;JS) \left[C_{01}^{11S} C_{10}^{11S} + C_{00}^{11S} C_{1-1}^{11S} \right]$$

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