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Theory of Resonance Pressure Broadening: Resolvent Operator Formalism and Classical Path Approximation†

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Abstract

The problem of resonance pressure broadening of spectral lines in monatomic gases is discussed using a resolvent operator formalism. A differential equation is developed to determine the resolvent, and it is shown how its solution for a limiting case yields the familiar classical path approximation for the translational motion of the atoms, and how quantum corrections may be systematically studied. Commonly used limiting cases within the classical path approximation (two-body static and impact approximations) are also exhibited as limiting cases, with methods for systematic evaluation of corrections. Closed form solutions are obtained for the two-body static and impact cases. The results are compared with available experimental data, and generally satisfactory agreement is obtained. Of some theoretical interest is the formalism, which embraces all the usual approximations and permits them to be studied together with corrections to them from a unified point of view. New results of more practical interest are the closed form solutions for the limiting cases, and the estimation of the lowest-order quantum corrections, which are appreciable under some experimental conditions.

1. *Introduction*

In recent years, there has been a revival of interest in the theory of the pressure broadening of spectral lines in gases. This problem is of some interest in itself and also provides an instructive illustration of various general techniques. Thus, Fano (1963) has considered pressure broadening as a prototype of relaxation, using a Liouville operator formalism, and this technique has been further applied by Ben-Reuven (1966a, b). Ross (1966) has considered the problem from the viewpoint of general many-body theory.

In all cases, the problem is to calculate the shape of the spectral line in terms of the properties of the isolated atoms or molecules, and of the pressure and temperature of the gas. From a formal point of view,

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most of the above-mentioned work is very general; but when actual numerical results are calculated, approximations must of course be made. In nearly all work which leads to numerical answers, the following approximations are made: First, one makes the 'classical path' approximation, i.e., one considers the translational motion of the atoms (or molecules) to be describable by classical mechanics. Second, the 'two-body' approximation is made. This means that interactions or collisions between different pairs of atoms are treated as independent of one another and (in some sense) additive in their effect on the line shape. As Fano (1963) has made clear, this can be thought of as expanding the line width in a power series in the density and keeping only the linear term. In this approximation, obviously, the width varies linearly with density. Beyond these approximations, there are two opposite limiting cases for which results can be obtained: if the atoms are moving very slowly, one can make the 'static' approximation, in which their positions are treated as fixed. In the opposite limit, where the velocities are very high, the 'impact' approximation of Baranger (1958a, b) may be used, in which the width can be shown to be expressible in terms of collision cross-sections.

In the present work, we concern ourselves with a particular case of considerable interest: the 'resonant' or 'self' broadening of the spectrum of a monatomic gas due to dipole–dipole interactions. This differs from the broadening by foreign gases more commonly treated in that the interaction can transfer the excitation from one atom to another. This means that no clear distinction can be made between perturbed atom and perturber; and that the interaction cannot be represented simply as an effective potential energy seen by the absorbing (or emitting) atom in its two states, as assumed in much of the theoretical work. The special properties of the resonant case have recently been emphasized by Bezzerides (1967). Earlier, a result which might be called the 'n-body theorem' had been proved (Reck *et al.*, 1965): For the resonant case, in the static limit, it is never permissable to use the two-body approximation except on the far wings of the line. Near the center (i.e., within a line width), interactions involving arbitrarily many atoms must be taken into account.

Despite these apparent difficulties, approximate calculations based on the two-body impact limit by Ali & Griem (1965, 6), Omont (1965, 6, 7), and Watanabe (1965a, b) led to good agreement with the experimental results of Kuhn & Vaughan (1964), and Vaughan (1965) on the emission spectra of helium. These experiments showed a linear dependence of the width on the density, in agreement with the two-body approximation, and the coefficient agreed rather well with

theory. On the other hand, the results of Lauristion & Welch (1951) on the alkali metals seem to require many-body effects to explain them (Reck, *et al.*, 1965).

From the experimental results, therefore, it would appear that the n-body theorem, which has been proved rigorously for the static limit, may not hold in the opposite (impact) limit. This is by no means obvious, however, as may be seen by comparing the situation in the resonant case with that of the nonresonant. In the case of nonresonant broadening by a foreign gas, let an excited atom A experience a collision with a perturber B. After the collision, the excitation will still be on A, since energy conservation forbids its transfer to B. Hence, except for a phase factor which disappears in the subsequent averaging, the initial internal state of the system is the same prior to a subsequent collision with another perturber C as it would have been if the A–B collision had never taken place. This is what permits one, in the nonresonant case, to treat successive collisions as independent. In the resonant case, however, B is an atom identical with A, and hence may very well have the excitation transferred to it in the collision. It follows that the initial state for a subsequent A–C collision will depend very much on what happened in the A–B collision, so it is not clear that they can be treated as independent. Ali & Griem (1965) attempt to avoid this difficulty by initially having the excitation shared symmetrically between A and B, and showing that after the collision it is still shared between them in the same way. This does not really avoid the problem, however. In order to treat a subsequent A–C collision in the same way, the excitation would have to be shared symmetrically between A and C, not A and B. Thus, it remains true that initial conditions for each collision depend critically on the previous ones. Nevertheless, we shall see that the conclusion is correct: In the impact limit, where velocities are large, it is permissible to use the two-body approximation.

The purpose of the present work is two-fold: First, and of most interest from a fundamental point of view, we wish to formulate the theory in a way which permits a systematic study of the approach to the classical path limit and the other limiting cases. For this purpose, a resolvent operator formalism is employed. It will be seen how the usual approximations appear as limiting cases, and it will be possible to study systematically their limits of validity and the corrections to them. It is hoped that the techniques employed here will be useful for other line-shape problems, and indeed for any problems involving the behavior of quantum mechanical systems in the vicinity of the classical limit.

Secondly, it is a peculiar property of the dipole–dipole, r^{-3} interaction that the two-body impact and static limits yield essentially the same formula for the line shape. In both cases, one finds a Lorentzian shape with half-width given by $a\mathcal{N}^2\mu^2$, where $\mathcal{N}$ is the density in atoms per cubic centimeter, $\hbar^{1/2}\mu$ is the dipole matrix element, and a is a dimensionless constant. Thus, the qualitative behavior of the line width is the same in both cases, and one can distinguish between them experimentally only if one has exact values for the coefficient a in the two cases. The question also arises of whether the two coefficients are equal. We have succeeded in obtaining closed-form solutions for both limiting cases. The coefficients are found not to be equal. Approximate evaluations of the coefficient for the impact case have been attempted before, both by simple perturbation theory (Ali & Griem, 1965, 6), and by rather elaborate machine calculations (Omont, 1965, 6, 7; Watanabe, 1965a, b). The exact answer turns out to be lower than the results of these calculations by somewhat less than 10%. The static case, as far as we are aware, has not been done in closed form before, although it is by far the easier of the two. Having done these calculations, we are able to compare the results with experiment, and find generally good agreement, with different approximations being applicable to different experimental situations.

Many of the results of this article are not new, though the unifying formalism enables one to see them from a new point of view. New results of practical interest are the closed form solutions and the study of the lowest order quantum corrections, especially for the impact limit.

The contents of the various sections may be summarized as follows:

Section 2 explains the notation and Hamiltonian used, and exhibits the basic formula for the complex refractive index in terms of the resolvent operator.

In Section 3, a differential equation is derived to determine the resolvent, and it is shown how to approach the classical limit and find a formal solution for that limit.

Section 4 takes up the two-body static and impact approximations.

Sections 5 and 6 discuss the closed-form solutions for the static and impact cases, respectively.

Sections 7 and 8 treat the corrections due to many-body effects and quantum effects, respectively.

In Section 9, the results are compared with experiment.

There is a brief concluding discussion in Section 10.

2. *Notation; Hamiltonian; Basic Formula for Refractive Index*

Apart from minor changes, the notation to be used is the same as that of Reck *et al.* (1965). Here, we recapitulate it briefly.

The system under consideration is an ideal, monatomic gas of N identical atoms, confined in a volume V. We are interested in the limit, $N,\ V \to \infty$, with the density $\mathcal{N} = N/V$ remaining constant. For the sake of definiteness, each atom is assumed to have a ^1S ground state and a triply degenerate ^1P excited level, the energy difference between the two being $\hbar\nu_0$. For the study of pure resonant effects, no other states need to be considered. Effects of quantum statistics are neglected.

The 'initial' state $|0\rangle$ is a state of the gas in which all atoms are in their ground states, and each atom A has momentum $\mathbf{p}_A = \hbar\mathbf{q}_A$. The momenta are distributed according to a Boltzmann distribution at some temperature T. The zero of energy is chosen to be that of the state $|0\rangle$.

States in which one or more atoms have become excited, and/or have acquired a momentum different from what they have in the state $|0\rangle$, are denoted by listing the excited atoms and/or their excess momenta in the ket symbol. Thus, $|A_i, \boldsymbol{\kappa}(A)\rangle$ denotes a state in which atom A has become excited, with polarization in the i-direction, and has a momentum $\hbar(\mathbf{q}_A + \boldsymbol{\kappa})$, with all other atoms being as they are in $|0\rangle$. The polarization direction is the direction of the dipole moment matrix element linking the excited state with the ground state: If we denote the dipole moment operator for atom A by $\hbar^{1/2}\boldsymbol{\mu}_A$, then

$$\langle A_i|\mu_{Aj}|0\rangle = \mu\,\delta_{ij}$$

the letter μ by itself denotes the value of the matrix element.

It was shown by Reck *et al.* (1965) that the transverse frequency- and wave number-dependent susceptibility $F(\nu, \boldsymbol{\kappa})$ (defined as 4π times the ordinary susceptibility) is given by

$$F(\nu, \boldsymbol{\kappa}) = -\frac{4\pi\mu^2}{V}\sum_A \varepsilon_j\langle A_j, \boldsymbol{\kappa}(A)|R(\nu)|A_k, \boldsymbol{\kappa}(A)\rangle\,\varepsilon_k, \qquad (2.1)$$

where $\boldsymbol{\epsilon}$ is a unit polarization vector perpendicular to $\boldsymbol{\kappa}$, and R is the resolvent operator expressed in frequency units:

$$R(\nu) = (\nu - \mathscr{H}/\hbar)^{-1}$$

The frequency ν is assumed to have a small positive imaginary part. The summation convention for repeated indices is used in (2.1) and throughout this paper. Equation (2.1) holds if $|\nu - \nu_0| \ll \nu_0$. is easily

derived if the radiation field is treated semiclassically. The derivation with a quantized field is given in Reck *et al.* (1965).

Since we have a Boltzmann distribution of momenta in the state $|0\rangle$, the sum in (2.1) can be replaced by an average:

$$F(\nu, \boldsymbol{\kappa}) = -4\pi\mathcal{N}\mu^2(\beta/\pi)^{3/2} \int \exp(-\beta q_A{}^2)\, \varepsilon_j \langle A_j, \boldsymbol{\kappa}(A)|R(\nu)|A_k, \boldsymbol{\kappa}(A)\rangle \times \\ \times\, \varepsilon_k d^3 q_A \tag{2.2}$$

where $\beta = \hbar^2/2mkT$. Equation (2.2) is the same as equation (3.3) of Reck *et al.* (1965), except that a misprint has been corrected ($\mathcal{N}/V$ instead of $\mathcal{N}$ appeared by mistake in the earlier article), and frequency rather than energy units are used both for R and μ^2.

Because of the randomness of directions, F is clearly independent of the direction of $\boldsymbol{\kappa}$:

$$F(\nu, \boldsymbol{\kappa}) = F(\nu, \kappa) \tag{2.3}$$

The observed complex refractive index $n(\nu)$ is found by solving

$$n^2(\nu) - 1 = F[\nu, n(\nu)\nu/c] \tag{2.4}$$

which normally requires analytic continuation to complex κ, i.e., leads to absorption.

In practice, for the problems in which we are interested, F is usually only a slowly varying function of κ in the region $\kappa \cong \nu/c \cong \nu_0/c$. In this case, we can define

$$F(\nu) = F(\nu, \nu/c) \cong F(\nu, \nu_0/c) \tag{2.5}$$

and then we have to good approximation

$$n^2(\nu) - 1 = F(\nu) \tag{2.6}$$

The Hamiltonian with respect to which the resolvent is taken is the total Hamiltonian of the system, including the quantized radiation field. It is a good approximation, however, to use just the Hamiltonian for the matter alone, and this will be done here. Accordingly, our Hamiltonian is

$$\mathcal{H} = \sum_A \frac{p_A{}^2}{2m} + \mathcal{H}_{\text{int}} + \hbar\mathcal{V} - \sum_A \hbar^2 q_A{}^2/2m \tag{2.7}$$

Here $\mathcal{H}_{\text{int}}$ is the internal Hamiltonian with eigenvalues $n\hbar\nu_0$ ($n =$ number of atoms excited). The last term is a constant added to insure that $\mathcal{H}|0\rangle = 0$. $\mathcal{V}$ represents the interatomic dipole–dipole interaction:

$$\mathcal{V} = \mu^2 \sum_{A \neq B} |A_j\rangle \frac{1}{r_{AB}^3}\left(\delta_{jk} - 3\frac{r_{AB_j} r_{AB_k}}{r_{AB}^2}\right)\langle B_k| \tag{2.8}$$

where $\mathbf{r}_{AB}$ is the vector separation between atoms A and B. In equation (2.8), $|A_j\rangle\langle B_k|$ operates on the internal state only (transferring excitation from B to A), and the rest of the operator involves the translational degrees of freedom. Referring to (2.1), we see that, since the number of excited atoms is conserved under the Hamiltonian (2.7), we need only consider states in which one atom is excited.

We now proceed to the problem of evaluating the necessary resolvent matrix elements.

3. *Differential Equation for Resolvent; Solution in Classical Path Approximation*

Writing out explicitly the integration over the translational degrees of freedom in the matrix element for R, we can write

$$\langle B_j, \boldsymbol{\varkappa}(A)|R(\nu)|C_k, \boldsymbol{\varkappa}(A)\rangle = \frac{1}{V^N}\int\cdots\int \langle B_j|\mathscr{R}(\nu)|C_k\rangle\, d^{3N}r \quad (3.1)$$

where

$$\mathscr{R}(\nu) = \exp(-i\Gamma)\left(\omega + \frac{\hbar}{2m}\sum_D \nabla_D{}^2 + \sum_D \frac{p_D{}^2}{2m\hbar} - \mathscr{V}\right)^{-1}\exp(i\Gamma) \quad (3.2)$$

with

$$\Gamma = \boldsymbol{\varkappa}\cdot\mathbf{r}_A + \frac{1}{\hbar}\sum_D \mathbf{p}_D\cdot\mathbf{r}_D \quad (3.3)$$

$$\omega = \nu - \nu_0$$

(We recall that all the states that concern us are eigenfunctions of $\mathscr{H}_{\text{int}}$ with eigenvalue $\hbar\nu_0$.) $\mathscr{R}(\nu)$ is a matrix in the internal states which is a function of the positions of the atoms. Evidently, from the definition of $\mathscr{R}$,

$$\left(\omega + \frac{\hbar}{2m}\sum_D \nabla_D{}^2 + \sum_D \frac{p_D{}^2}{2m\hbar} - \mathscr{V}\right)[\exp(i\Gamma)\,\mathscr{R}(\nu)] = \exp(i\Gamma) \quad (3.4)$$

We now combine (3.3) and (3.4), carry out the indicated differentiations in (3.4), and cancel a factor $\exp(i\Gamma)$. The result is

$$\left(\omega - \boldsymbol{\varkappa}\cdot\mathbf{v}_A + \frac{\hbar}{2m}\kappa^2 + i\sum_D \mathbf{v}_D\cdot\nabla_D + \frac{i\hbar}{m}\boldsymbol{\varkappa}\cdot\nabla_A + \frac{\hbar}{2m}\sum_D \nabla_D{}^2 - \mathscr{V}\right)\mathscr{R} = 1 \quad (3.5)$$

where $\mathbf{v}_D = \mathbf{p}_D/m$ is the velocity of atom D.

Equation (3.5) is the fundamental differential equation which we

shall use to approximately determine $\mathscr{R}$, and through it the desired matrix elements of R.

The notation up to this point has been arranged in such a way as to facilitate the passage to the classical limit for the translational degrees of freedom in a way which is meaningful for our problem. Ultimately, we want to calculate the refractive index at a given frequency (not given photon energy) for a gas with a given momentum (not wave number) distribution. Therefore, as we let $\hbar$ approach zero, we want ω, κ, and all the $\mathbf{p}_D$ to remain constant. Also, to get the right answer for the effect of interatomic interaction on the line shape, we want this interaction, *expressed in frequency units*, i.e., $\mathscr{V}$, to remain constant as $\hbar$ approaches zero. If we held constant the interaction in energy units, then the line shape as a function of frequency would become infinitely broad, and our result would not correspond to the true physical situation. The reader will observe that with our notation all these requirements are satisfied if we simply let $\hbar$ approach zero formally in equation (3.5). There is no need to think about these matters any more, the notation will do that for us.

We now develop an expansion of (3.5) near the classical limit. First, for convenience, define

$$\lambda = \omega - \boldsymbol{\kappa}.\mathbf{v}_A \tag{3.6}$$

Now expand $\mathscr{R}$ as

$$\mathscr{R} = \mathscr{R}_0 + \hbar\mathscr{R}_1 + \cdots \tag{3.7}$$

Combining (3.5), (3.6), and (3.7), we find

$$\left(\lambda + i\sum_D \mathbf{v}_D.\nabla_D - \mathscr{V}\right)\mathscr{R}_0 = 1 \tag{3.8}$$

$$\left(\lambda + i\sum_D \mathbf{v}_D.\nabla_D - \mathscr{V}\right)\mathscr{R}_1 = -\left(\frac{\kappa^2}{m} + \frac{i}{m}\boldsymbol{\kappa}.\nabla_A + \frac{1}{2m}\sum_D \nabla_D{}^2\right)\mathscr{R}_0 \tag{3.9}$$

etc.

Equation (3.8) corresponds to the 'classical path approximation,' while (3.9) determines the lowest-order correction to it. For the present (until Section 8), we confine our attention to (3.8).

The solution of (3.8) is facilitated if we introduce new coordinates in the $3N$-dimensional configuration space. Let one of the new coordinates be

$$\tau = \left(\sum_D v_D{}^2\right)^{-1} \sum_D \mathbf{v}_D.\mathbf{r}_D \tag{3.10}$$

The definition of the other $(3N-1)$ coordinates is arbitrary, except that they should be orthogonal to τ, and to each other. Thus, let a typical one be

$$\eta = \sum_D \boldsymbol{\alpha}_{\eta D} \cdot \mathbf{r}_D \tag{3.11}$$

such that

$$\sum_D \boldsymbol{\alpha}_{\eta D} \cdot \mathbf{v}_D = 0$$

$$\sum_D \boldsymbol{\alpha}_{\eta D} \cdot \boldsymbol{\alpha}_{\eta' D} = 0, \qquad \eta \neq \eta' \tag{3.12}$$

In this coordinate system, (3.8) becomes

$$\left[\lambda + i\frac{\partial}{\partial \tau} - \mathscr{V}(\tau, \eta)\right] \mathscr{R}_0(\tau, \eta) = 1 \tag{3.13}$$

The solution of (3.13) may be expressed in terms of the quantity $U_\eta(\tau|\tau_0)$, defined by the conditions

$$U_\eta(\tau_0|\tau_0) = 1 \tag{3.14}$$

$$i\frac{\partial}{\partial \tau} U_\eta(\tau|\tau_0) = \mathscr{V}(\tau, \eta)\, U_\eta(\tau|\tau_0) \tag{3.15}$$

U_η is seen to be simply the time-displacement operator under the interaction $\hbar\mathscr{V}$ when the system moves from the configuration (η, τ_0) to (η, τ). It is given formally by

$$U_\eta(\tau|\tau_0) = \mathscr{T} \exp\left[-i \int_{\tau_0}^{\tau} \mathscr{V}(\tau', \eta)\, d\tau'\right] \tag{3.16}$$

where $\mathscr{T}$ denotes time ordering. Clearly,

$$U_\eta(\tau|\tau_0) = U_\eta(\tau|\tau_1)\, U_\eta(\tau_1|\tau_0) \tag{3.17}$$

for any τ_1, and U_η is unitary if $\mathscr{V}$ is Hermitian (which it is):

$$U_\eta{}^+(\tau|\tau_0) = U_\eta^{-1}(\tau|\tau_0) = U_\eta(\tau_0|\tau) \tag{3.18}$$

We now seek a solution of (3.13) of the form

$$\mathscr{R}_0(\tau, \eta) = U_\eta(\tau|\tau_0)\, \rho(\tau, \eta) \exp(i\lambda\tau) \tag{3.19}$$

Substituting (3.19) into (3.13), one finds

$$iU_\eta(\tau|\tau_0)\left[\frac{\partial}{\partial \tau}\rho(\tau, \eta)\right] \exp(i\lambda\tau) = 1 \tag{3.20}$$

a solution of which may be found using (3.18):

$$\rho(\tau, \eta) = \frac{1}{i} \int_{-\infty}^{\tau} U_\eta(\tau_0|\tau') \exp(-i\lambda\tau')\, d\tau' \tag{3.21}$$

Now, using (3.17), (3.19) and (3.21), we find

$$\mathscr{R}_0(\tau, \eta) = \frac{1}{i} \int_{-\infty}^{\tau} U_\eta(\tau|\tau') \exp[i\lambda(\tau - \tau')]\, d\tau' \tag{3.22}$$

$$= \frac{1}{i} \int_{0}^{\infty} U_\eta(\tau|\tau - t) \exp(i\lambda t)\, dt \tag{3.23}$$

where $t = \tau - \tau'$. Note that U, $\mathscr{R}$, ρ are all matrices, so the correct order of factors is important in equations (3.18–3.23).

In the original coordinate system, (3.23) becomes

$$\mathscr{R}_0(\mathbf{r}) = \frac{1}{i} \int_{0}^{\infty} U(\mathbf{r}|\mathbf{r} - \mathbf{v}t) \exp(i\lambda t)\, dt \tag{3.24}$$

The U operator in (3.24) is just the time-displacement operator *for the internal states only* for a process in which the system is translated rigidly with constant velocity $\mathbf{v}$ ($\mathbf{v}_D$ for each atom D) from an initial configuration $(\mathbf{r} - \mathbf{v}t)$ to a final configuration $(\mathbf{r})$, while being acted upon by the interaction $\hbar\mathscr{V}$. In retrospect, the result is not surprising: The resolvent is well known to be related by a Laplace transform to the time-displacement operator, as in (3.24), and in the classical path approximation the operators for the translational coordinates are replaced by c-number functions of the time. Note that the formalism requires that all the velocities be treated as constant. It would be inconsistent in this approximation to try to correct for accelerations experienced by the atoms because of the interaction.

We have neglected an arbitrary constant of integration in (3.21), but it is easily seen that it is correct to set it equal to zero. In the limit of weak interaction, or of very large λ, $\mathscr{R}_0$ should approach λ^{-1}, which it does with this choice of integration constant.

According to (3.1), (3.7) and (3.24), the matrix element of R_0, the classical path limit of R, is obtained by averaging a matrix element of (3.24) over configuration space:

$$\langle B_j, \boldsymbol{\varkappa}(A)|R_0|C_k, \boldsymbol{\varkappa}(A)\rangle = \frac{1}{V^N} \int \cdots \int \langle B_j|\mathscr{R}_0(\mathbf{r})|C_k\rangle\, d^{3N}r \tag{3.25}$$

Equations (3.24) and (3.25) provide us with formal expressions for the matrix elements which we need (and many others besides) in

classical path approximation. In order to get actual answers, however, it is necessary to study further limiting cases within the classical path approximation. This we proceed to do in the next section.

4. *Limiting Cases and Approximations*

4.1. *The Two-Body Approximation*

Intuitively, this approximation means that interactions or collisions between different pairs of particles are treated as independent. More formally, it has been expressed (Fano, 1963; Reck *et al.*, 1965) as keeping the linear term in an expansion of the linewidth in powers of the density. Actually, these two statements of the approximation are not quite equivalent in all cases (as we shall see presently), but they are equivalent in the limiting cases which we shall be studying in most detail. We use the former statement, and now proceed to formulate it more precisely.

It is clear from equation (2.1) that the only matrix elements of R that we need to consider are those which are diagonal with respect to the excited atom (i.e., $\langle A_i|R|A_j\rangle$ but not $\langle A_i|R|B_j\rangle$). Now consider the development of the operator U in (3.25) as the gas goes from the initial configuration $(\mathbf{r} - \mathbf{v}t)$ to the final one $(\mathbf{r})$. The matrix elements that we need are those representing processes in which the excitation is initially on atom A, and is again on A at the end of the process. If the gas is dilute enough, one may assume that no more than one atom is very close to A at any given time, so that at each time the development of U is dominated by the interaction of A with the atom closest to it at the time. Thus, the U operator becomes a product of partial U operators representing the interaction of A with all those other atoms which pass close to it, ordered chronologically. Moreover, if one excludes from consideration processes in which the excitation is transferred from A to some other atom B and subsequently carried back to A by a third atom, only that part of each partial U operator which leaves the excitation on A need be kept. Furthermore, when one averages over directions of motion of the colliding atoms (as must be done eventually), each partial U operator (as well as the full one) becomes a scalar as far as polarization direction is concerned; this causes them all to commute, so the time ordering between the partial U operators need not be kept track of.† As for the atoms which never

† Strictly speaking, there is still a preferred direction, namely that of $\mathbf{v}_A$. Since it is the same (after averaging) for all the incident atoms, this does not change the conclusion that the averaged partial U operators commute. We will ignore this effect, since it plays no role in the limiting cases which are our prime concern.

pass close to A, they contribute practically nothing anyway, so it does no harm to include them in the same way as the others. These ideas may be expressed mathematically by writing

$$\langle A_i|U(\mathbf{r}|\mathbf{r}-\mathbf{v}t)|A_j\rangle = \delta_{ij}\prod_{D\neq A} U_D(\mathbf{r}_{AD},\mathbf{v}_{AD},t) \tag{4.1.1}$$

$$U_D(\mathbf{r}_{AD},\mathbf{v}_{AD},t) = \tfrac{1}{3}\langle A_k|U_{AD}(\mathbf{r}_{AD},\mathbf{v}_{AD},t)|A_k\rangle \tag{4.1.2}$$

with

$$U_{AD}(\mathbf{r}_{AD},\mathbf{v}_{AD},t) = \mathscr{T}\exp\left\{-i\int_0^t \mathscr{V}_{AD}[\mathbf{r}_{AD}-\mathbf{v}_{AD}(t-\tau)]\,d\tau\right\} \tag{4.1.3}$$

$\mathscr{V}_{AD}$ represents the terms coupling A with D in (2.8). We note that all the U_D are real, since only the even terms in the expansion of the exponential in (4.1.3) are diagonal. Now, combining (3.1), (3.24), (3.25) and (4.1.1), we find

$$\langle A_i,\boldsymbol{\varkappa}(A)|R_0|A_j,\boldsymbol{\varkappa}(A)\rangle = \delta_{ij}\frac{1}{V^N}\int\cdots\int d^{3N}\mathbf{r}\,\frac{1}{i}\int_0^\infty \prod_{D\neq A} U_D(\mathbf{r}_{AD},\mathbf{v}_{AD},t)\times$$
$$\times\exp(i\lambda t)\,dt \equiv \delta_{ij}R_0 \tag{4.1.4}$$

The integration over r_A gives a factor V. We also note that if r_{AD} is large enough (i.e., for most of the volume), U_D is very nearly unity. Therefore, define

$$\int (1-U_D)\,d^3r_{AD} = u(v_{AD},t) \tag{4.1.5}$$

Then, from (4.1.4), (4.1.5), we find

$$R_0 = \frac{1}{i}\int_0^\infty \prod_{D\neq A}\left[1-\frac{u(v_{AD},t)}{V}\right]\exp(i\lambda t)\,dt \tag{4.1.6}$$

In the limit as $N,\ V\to\infty$, (4.1.6) becomes

$$R_0 = \frac{1}{i}\int_0^\infty \exp[i\lambda t - \mathscr{N}\bar{u}(t)\,dt \tag{4.1.7}$$

where

$$\bar{u}(t) = \frac{1}{N-1}\sum_{D\neq A} u(v_{AD},t)$$

is the average of u over velocities. Equation (4.1.7) represents the two-body approximation in its most general form (commensurate with the classical path approximation).

It will be helpful to study the properties of u briefly by dimensionless analysis. Suppose we suppress the subscript (AD) in (4.1.3), choose our z-axis in the direction of $\mathbf{v}$, and substitute $\zeta = v\tau$. We find

$$U(\mathbf{r}, \mathbf{v}, t) = \mathscr{T} \exp\left[-\frac{i}{v}\int_0^{vt} \mathscr{V}(x, y, z - vt + \zeta)\, d\zeta\right] \tag{4.1.8}$$

In equation (4.1.8), the interaction $\mathscr{V}$ is proportional to μ^2, and appears divided by v. The only other parameters appearing are x, y, z, and vt, of which the first three disappear when we integrate to find u. We conclude that u depends on v, t as

$$u(v, t) = u(\mu^2/v, vt) \tag{4.1.9}$$

Of the quantities appearing in (4.1.9), μ^2/v has the dimensions of an area, vt is a length, and u must be a volume. It follows on dimensional grounds that u can be written as

$$u(v, t) = \mu^2 t f(\mu^2/v^3 t^2) \tag{4.1.10}$$

where f is some dimensionless function of a dimensionless variable. Equation (4.1.10) will be useful to us in later sections.

We notice from (4.1.10) that $\bar{u}(t)$ may, in general, be quite a complicated function of t, causing R_0 to be a complicated function of $\mathscr{N}$ when the integration in (4.1.7) is carried out. This is the basis for the statement made at the outset of this section, that the two-body approximation as formulated here is not always equivalent to expanding in $\mathscr{N}$ and keeping the linear term. Corrections to the two-body approximation will be discussed in Section 7.

4.2. *Static Approximation*

If vt is sufficiently small, one may consider $\mathscr{V}$ to be constant all along the path of integration in (3.16). In that case,

$$U(\mathbf{r}|\mathbf{r} - \mathbf{v}t) = \exp\left[-i\mathscr{V}(\mathbf{r})\, t\right] \tag{4.2.1}$$

Combining (3.24) and (4.2.1), we find

$$\mathscr{R}_0(\mathbf{r}) = [\lambda - \mathscr{V}(\mathbf{r})]^{-1} \tag{4.2.2}$$

The integration in (3.25) is now just an average, so

$$\langle B_j, \kappa(A)|R_0|C_k, \kappa(A)\rangle = \overline{\langle B_j|(\lambda - \mathscr{V})^{-1}|C_k\rangle} \tag{4.2.3}$$

The validity criterion for (4.2.2) may be written symbolically as

$$vt|\nabla(\ln \mathscr{V})| \ll 1 \tag{4.2.4}$$

In order to use (4.2.1) in (3.24) to get (4.2.2), it must be assumed that (4.2.4) holds for all t which contribute appreciably to the integral in (3.24), i.e., for all $t \lesssim \lambda^{-1}$. Accordingly, the validity criterion for (4.2.2), (4.2.3) is

$$v\lambda^{-1}|\nabla(\ln \mathscr{V})| \ll 1 \tag{4.2.5}$$

It is seen that the static approximation is always valid on the far wings of the line, and always breaks down near the center.

4.3. *Static Two-Body Approximation*

The approximations of Sections 4.1 and 4.2 may be combined by making the static approximation (4.2.1) in (4.1.2) and (4.1.3). The result is

$$U_{AD} = \exp[-i\mathscr{V}(\mathbf{r}_{AD})\, t] \tag{4.3.1}$$

Combining (4.1.2), (4.1.5) and (4.3.1), we find

$$u = \int \{1 - \tfrac{1}{3}\langle A_j|\exp[-i\mathscr{V}(\mathbf{r})\, t]|A_j\rangle\} d^3 r \tag{4.3.2}$$

In the language of equation (4.1.10), the assumption that vt is small means that the argument of f in (4.1.10) goes to infinity. Thus, if we make the definition (anticipating the existence of the limit, to be verified in the next section):

$$\lim_{x\to\infty} f(x) \equiv \frac{\pi^2}{2} k_s \tag{4.3.3}$$

then we find from (4.1.7), (4.1.10) and (4.3.3) that

$$R_0 = \left(\lambda + i\mathscr{N}\frac{\pi^2}{2} k_s \mu^2\right)^{-1} \tag{4.3.4}$$

In this approximation, therefore, the pressure-broadened line is Lorentzian, becoming a Voigt profile (convolution of Lorentzian with Gaussian) when the average of equation (2.2) is performed with the aid of (3.6). The parameter k_s (s = static) has been defined so as to coincide with the broadening parameter k used by Kuhn & Vaughan (1964), and Vaughan (1966).

The validity criteria for this approximation will be discussed jointly with those of its opposite, the two-body impact approximation, at the end of Section 4.4.

4.4. *Two-Body Impact Approximation*

Here we consider the opposite limit to (4.3.3), in which the argument of f in (4.1.10) goes to zero; in other words, v is considered to be very large.

Now, if l is some measure of the distance over which U changes appreciably as a function of z in (4.1.8), we see that U assumes the following limiting forms:

$$\begin{aligned} U(\mathbf{r}, \mathbf{v}, t) &= 1, (z - vt) \gg l \\ &= 1, z \ll -l \\ &= \mathscr{S}(x, y, v), z \gg l, (z - vt) \ll -l \end{aligned} \tag{4.4.1}$$

Here $\mathscr{S}$ is the scattering matrix, defined by

$$\mathscr{S}(x, y, v) = \mathscr{T} \exp\left[-\frac{i}{v} \int_{-\infty}^{\infty} \mathscr{V}(x, y, z)\, dz\right] \tag{4.4.2}$$

If $vt \gg l$, then we will be in error only for a negligibly small fraction of the total volume if we replace the $\gg$ and $\ll$ in (4.4.1) by $>$ and $<$. If we do this, (4.4.1) gives us U for the entire volume, and u can easily be evaluated in terms of $\mathscr{S}$. If we define

$$\mathscr{S} = 1 + \Lambda$$

then we find from (4.1.5) and (4.4.1):

$$u(v, t) = -vt \int \tfrac{1}{3} \langle A_j | \Lambda | A_j \rangle\, dx\, dy \tag{4.4.3}$$

But it is easily shown (Ali & Griem, 1965) from the unitarity of $\mathscr{S}$ that the integral in (4.4.3) is just $-\frac{1}{2}\sigma$, where σ is the average total cross-section. It follows that, in this approximation,

$$u(v, t) = vt \frac{\sigma}{2} \tag{4.4.4}$$

In the language of (4.1.10), we can define

$$f(0) = \tfrac{1}{2}\pi^2 k_i \tag{4.4.5}$$

Now, from (4.1.7), (4.1.10), (4.4.4) and (4.4.5), we find

$$\sigma = \pi^2 k_i \mu^2 / v \tag{4.4.6}$$

and

$$R_0 = \left(\lambda + i\mathscr{N} \frac{\sigma}{2} v\right)^{-1} \tag{4.4.7}$$

The form of (4.4.6) could, of course, have been derived on purely dimensional grounds.

We notice that (4.4.7) combined with (4.4.6) is the same as (4.3.4), except that k_i appears instead of k_s.†

As for validity criteria, we see from (4.1.10) and (4.3.3) that the static approximation (given the two-body approximation) holds for U if

$$\left(\frac{\mu^2}{v^3 t^2}\right) \gg 1$$

or, referring to (4.4.6), if

$$\frac{\sigma}{(vt)^2} \gg 1, \qquad vt \ll \sqrt{\sigma} \tag{4.4.8}$$

Conversely, the impact result holds if

$$vt \gg \sqrt{\sigma} \tag{4.4.9}$$

so we see that $\sqrt{\sigma}$ plays the role of l in (4.4.1), which is not surprising. To get the criterion in terms of frequency, we substitute $t \sim \lambda^{-1}$ in (4.4.9), and find

$$v\lambda^{-1} \gg \sqrt{\sigma} \tag{4.4.10}$$

If (4.4.10) is to hold for λ of the order of the linewidth, we must have, according to (4.4.7),

$$\mathcal{N}\sigma v \ll v/\sqrt{\sigma} \tag{4.4.11}$$

which is just the familiar requirement (Baranger, 1958) that the rate of collisions must be much less than the reciprocal lifetime of a collision. When this holds, the impact approximation may be used for the most important part of the line, namely from the center out to several times the width. It is *never* correct to use it for the entire line.

5. *Closed Form Solution: Static Two-Body Approximation*

The solution for this case can be found by the methods of Reck *et al.* (1965), but we use another method, based on the work of the previous section.

According to (4.3.1), and omitting the subscript (AD) for simplicity, we must evaluate

$$\exp\left[-i\mathscr{V}(\mathbf{r})\, t\right]$$

where $\mathscr{V}(\mathbf{r})$ is given by the terms in (2.8) involving a particular pair, say A and B.

† The fact that v drops out of the limiting expressions for u justifies our neglect of the v-dependence of the partial U operators mentioned in the footnote to page 327.

Now it is convenient to define

$$\mathscr{W}(\mathbf{r}) = \frac{\mu^2}{r^3}\left(\delta_{ij} - 3\frac{r_i r_j}{r^2}\right)(|A_i\rangle\langle A_j| + |B_i\rangle\langle B_j|)$$
$$\mathscr{Y} = |A_k\rangle\langle B_k| + |B_k\rangle\langle A_k| \tag{5.1}$$

in terms of which it is easily seen that

$$\mathscr{V}(\mathbf{r}) = \mathscr{W}(\mathbf{r})\,\mathscr{Y}$$

In this representation of $\mathscr{V}$, the excitation transfer is contained in $\mathscr{Y}$, while the dependence on $\mathbf{r}$, and on polarization, is represented by $\mathscr{W}(\mathbf{r})$. We now have

$$\exp[-i\mathscr{V}(\mathbf{r})t] = \cos\mathscr{W}(\mathbf{r})t - i\mathscr{Y}\sin\mathscr{W}(\mathbf{r})t \tag{5.2}$$

To evaluate the trace appearing in (4.3.2), we choose the z-axis in the direction of $\mathbf{r}$. In this coordinate system,

$$\langle A_z|\exp(-i\mathscr{V}t)|A_z\rangle = \cos\frac{2\mu^2}{r^3}t$$
$$\langle A_y|\exp(-i\mathscr{V}t)|A_y\rangle = \langle A_x|\exp(-i\mathscr{V}t)|A_x\rangle = \cos\frac{\mu^2}{r^3}t$$

so equation (4.3.2) becomes

$$u = \int\left\{1 - \frac{1}{3}\left(\cos\frac{2\mu^2}{r^2}t + 2\cos\frac{\mu^2}{r^2}t\right)\right\}d^3r$$
$$= 4\pi\int_0^\infty\left\{1 - \frac{1}{3}\left(\cos\frac{2\mu^2}{r^3}t + 2\cos\frac{\mu^2}{r^3}t\right)\right\}r^2\,dr$$
$$= \tfrac{8}{9}\pi^2\mu^2 t \tag{5.3}$$

The integration is conveniently done by making the change of variables $y = \mu^2/r^3$.

Comparing equations (4.1.10), (4.3.3), (4.3.4) and (5.3), we see that

$$k_s = 16/9 \tag{5.4}$$

This completes the solution for the static two-body case. The result is a Lorentzian line (Voigt profile after velocity averaging) described by (4.3.4) with the parameter k_s given by (5.4).

6. *Closed Form Solution: Two-Body Impact Approximation*

6.1. *Preliminaries: Classical Path Versus Partial-Wave Method*

In the impact approximation, the calculation of the line shape reduces to that of finding the average total scattering cross-section.

Because of the classical path approximation, only the classical limit of this cross-section need be considered. Up to now, the theory has been developed in terms of the scattering matrix given by (4.4.2). However, a closed form solution is most easily obtained using a partial-wave expansion with passage to the classical limit. For purposes of orientation, we present in this section some considerations on the relation between the two methods. Most of this material is not new (Landau & Lifshitz, 1965); nevertheless, it seems advisable to review it from the point of view of our particular problem, especially since the partial wave method seems to be little used in line shape theory up to now.

Consider the two-body scattering problem (with internal degrees of freedom permitted), in the center-of-mass system, with the incident particle having momentum p directed along the z-axis, and the interaction being represented by $\hbar\mathscr{V}$. The equation satisfied by the wave function (in general a vector in the space of the internal coordinates) is

$$\left(-\frac{\hbar}{2m}\nabla^2 + \mathscr{V}\right)\psi = \frac{p^2}{2m\hbar}\psi \tag{6.1.1}$$

where m is now the reduced mass. If we substitute

$$\psi = \chi \exp(ipz/\hbar)$$

we find

$$\left(-iv\frac{\partial}{\partial z} + \mathscr{V} - \frac{\hbar}{2m}\nabla^2\right)\chi = 0$$

or to lowest order in $\hbar$

$$iv\frac{\partial}{\partial z}\chi = \mathscr{V}\chi$$

Now if we write

$$\chi(x, y, z) = U_{xy}(z|z_0)\,\chi(x, y, z_0)$$

then we find

$$U_{xy}(z|z_0) = \mathscr{T}\exp\left[-\frac{i}{v}\int_{z_0}^{z}\mathscr{V}(x, y, z')\,dz'\right] \tag{6.1.2}$$

The scattering is given by letting the arguments of U go to plus and minus infinity, i.e., by

$$\mathscr{S}_{xy} = U_{xy}(\infty|-\infty)$$

which is evidently the same as (4.4.2). It is evident that the cross-section is given by

$$\sigma = \sum_j \iint |\chi_j(x, y, \infty) - \chi_j(x, y, -\infty)|^2 \, dS$$

where the integral goes over some surface at infinity. This is usually taken to be a sphere, but (since there is no backward scattering in this limit) may equally well be a plane at positive infinity. (Recall that the interaction in energy units is infinitesimally small, so that all scattering is through very small angles; thus, there is really no difference between sphere and plane.) The sum is over internal states. Now if the initial internal state is denoted by o, then

$$\chi_j(-\infty) = \delta_{jo},$$

and we have

$$\sigma = \sum_j \iint |\mathscr{S}_{jo} - \delta_{jo}|^2 \, dx \, dy \tag{6.1.3}$$

Because

$$\sum_j |\mathscr{S}_{jo}|^2 = 1$$

(unitarity), we have

$$2 \operatorname{Re}(1 - \mathscr{S}_{oo}) = \sum_j |\mathscr{S}_{jo} - \delta_{jo}|^2$$

from which follows the relation between cross-section and diagonal element of A used previously to get equation (4.4.4).

To see the connection with the partial-wave method, consider the special case where there are no internal degrees of freedom, and we have spherical symmetry: $\mathscr{V} = F(r)$. Then $\mathscr{S}$ is a function only of the impact parameter $b = (x^2 + y^2)^{1/2}$, and can be expressed as

$$\begin{aligned} \mathscr{S}(b) &= \exp\left\{-\frac{i}{v} \int_{-\infty}^{\infty} F[\sqrt{(b^2 + z^2)}] \, dz\right\} \\ &= \exp\left[-\frac{2i}{v} \int_b^{\infty} \frac{rF(r) \, dr}{\sqrt{(r^2 - b^2)}}\right] \end{aligned} \tag{6.1.4}$$

The factor of 2 appears in the second expression because the path is traversed twice in r, once coming in and once going out.

If we were doing the same problem by partial waves, we would expand

$$\psi = \sum_l P_l(\cos\theta) \frac{\chi_l(r)}{r}$$

and arrive at the equation

$$-\frac{\hbar}{2m}\chi_l'' + \frac{\hbar l(l+1)}{2mr^2}\chi_l + F(r)\chi_l = \frac{p^2}{2m\hbar}\chi_l \tag{6.1.5}$$

In order to approach the classical limit by means of the WKB approximation, we first set $\hbar l = L$ (the classical angular momentum, which is to be held constant), and make the substitution

$$\chi_l(r) = \exp[i\lambda(r)/\hbar]$$

Equation (6.1.5) would then take the form

$$(\lambda')^2 - i\hbar\lambda'' + \frac{L^2}{r^2} + \frac{\hbar L}{r^2} + 2m\hbar F = p^2 \tag{6.1.6}$$

The next step is to expand λ in powers of $\hbar$:

$$\lambda = \lambda_0 + \hbar\lambda_1 + \cdots$$

In zero order, one has

$$(\lambda_0')^2 = p^2 - L^2/r^2$$

$$\lambda_0(r) = \int_b^r p\sqrt{[1 - b^2/(r')^2]}\,dr' + C \tag{6.1.7}$$

in which the integration constant C is determined by the boundary conditions at the turning point $b = p/L$, which is, of course, the same as the classical impact parameter for momentum p and angular momentum L.

Taking the terms of first order in $\hbar$ in (6.1.6), we find

$$2\lambda_0'\lambda_1' - i\lambda_0'' + L/r^2 + 2mF = 0 \tag{6.1.8}$$

From (6.1.7) and (6.1.8), we obtain

$$\lambda_1' = \tfrac{1}{2}(p^2 - L^2/r^2)^{-1/2}\left\{\frac{iL^2}{r^2\sqrt{(p^2 - L^2/r^2)}} - \frac{L}{r^2} - 2mF\right\} \tag{6.1.9}$$

The phase *shift* is the difference between the phase at infinity and what it would be if there were no interaction. Mathematically speaking, to this approximation,

$$\begin{aligned}\delta &= \mathrm{Re}\,[\lambda_1(\infty) - \lambda_1(\infty)|F = 0] \\ &= -\int_b^\infty \frac{mF\,dr}{\sqrt{(p^2 - L^2/r^2)}} = -\frac{1}{v}\int_b^\infty \frac{rF\,dr}{\sqrt{(r^2 - b^2)}}\end{aligned} \tag{6.1.10}$$

Effects due to changes in the boundary conditions at b are easily seen to be of a higher order of magnitude, so (6.1.10) gives us the phase shift to lowest order in $\hbar$.

With the aid of the correspondence $L = \hbar l = bp = b\hbar k$, we see from (6.1.4) and (6.1.10) that

$$\mathscr{S}(b) = \exp(2i\delta_l)$$

with the cross-section being given by

$$\sigma = 2\pi \int_0^\infty b|\exp(2i\delta_l) - 1|^2 db$$

$$= \frac{4\pi}{k^2} \int_0^\infty 2l \sin^2 \delta_l \, dl \tag{6.1.11}$$

This differs from the usual expression

$$\sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \delta_l$$

only in that the sum is replaced by an integral, and 1 is neglected compared with l.

In partial-wave language, then, the classical path approximation corresponds to taking the lowest order WKB approximation for the phase shift, and replacing the usual sum by an integral. The relation between impact parameter and angular momentum is just the classical one, $\hbar l = L = bp$, and the scattering matrix is related to the phase shift by

$$\mathscr{S}(b) = \exp(2i\delta_l) \tag{6.1.12}$$

Equation (6.1.12) expresses the fact, familiar in partial-wave theory, that the ratio of the outgoing amplitude for a given angular momentum to what it would be in the absence of interaction is just $\exp(2i\delta_l)$.

The problem which we have to solve is complicated by the presence of internal degrees of freedom, but the same general principles apply. We now proceed to set up this problem and solve it.

6.2. *Setting Up the Problem*

We have two kinds of internal degrees of freedom to deal with: the one which tells us which atom is excited, and the one designating polarization. The former is removed quite easily by taking symmetric and antisymmetric linear combinations. If we define

$$|j_\pm\rangle = \sqrt{\tfrac{1}{2}}(|A_j\rangle \pm |B_j\rangle) \tag{6.2.1}$$

then

$$\langle j_\pm|\mathscr{V}|k_\pm\rangle = \pm\frac{\mu^2}{r^3}\left\{\delta_{jk} - 3\frac{r_j r_k}{r^2}\right\} \tag{6.2.2}$$

and there are no matrix elements connecting (+) with (−) states. They can therefore be treated separately. We consider only the symmetric (+) combination for the present. The results for the (−) are obviously the same, with μ^2 being replaced by $-\mu^2$.

Insofar as this is possible, we want to expand our wave function in eigenfunctions of conserved quantities, which can then be treated separately. We have already done this in (6.2.1), choosing eigenfunctions of $\mathscr{Y}$, defined in (5.1). Normally, in partial wave theory, one expands in eigenfunctions of orbital angular momentum, but that will not quite do here, since the interaction couples the orbital angular momentum to the internal angular momentum S, which behaves formally like a spin of one (because we deal with a P state). The total angular momentum J, however, is conserved, along with its component in the z-direction (chosen parallel to the incident velocity). Accordingly, it is better to choose our internal states as eigenfunctions of S_z with eigenvalues $m_S = 0, \pm 1$, than as states with a definite direction of polarization. We then combine these with orbital states to build eigenfunctions of J^2, J_z, with eigenvalues, $J(J+1)$ and m_J.

In terms of the internal angular momentum S, the interaction (6.2.2) takes the form

$$\mathscr{V} = \frac{\mu^2}{r^3}\left[3\frac{(\mathbf{r}\cdot\mathbf{S})^2}{r^2} - 2\right] \tag{6.2.3}$$

Our incident states are plane waves multiplied by internal states; they therefore have $m_J = 0, \pm 1$, since the z-component of orbital angular momentum is zero. Since m_J is conserved, therefore, we need only consider states with $m_J = 0, \pm 1$.

It is also useful to have some idea of the magnitudes of angular momentum that we will be most interested in. We know from the dimensional analysis that

$$\sigma \sim \mu^2/v \tag{6.2.4}$$

while we have from the phase shift formula that

$$\begin{aligned}\sigma &= \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l \\ &\sim \frac{4\pi\hbar^2}{m^2v^2}\int 2l\sin^2\delta_l\, dl \sim \frac{4\pi\hbar^2}{m^2v^2}\bar{l}^2\end{aligned} \tag{6.2.5}$$

where $\bar{l}$ is some rough maximum l for which the phase shift is appreciable. From (6.2.4) and (6.2.5), we see that the values of l which contribute appreciably are those for which

$$l \sim \frac{m\mu\sqrt{v}}{\hbar} \gg 1 \tag{6.2.6}$$

We see that the l of interest are very large in the classical limit, and that what remains constant is $L = \hbar l$.

We must now express the eigenfunctions of total angular momentum in terms of those for orbital and internal angular momentum. This is easily done by standard angular momentum theory. We list below the expressions for states with definite l, J, m_J (denoted by $|l,J,m_J\rangle$) in terms of direct products of orbital states with definite l, m_l (denoted by $|l,m_l\rangle$) and internal states with definite m_S ($|m_S\rangle$). Each expression is followed by its limit for large l. The results are as follows:

$$\begin{aligned}|l,l+1,1\rangle = &\sqrt{\left[\frac{l+2}{2(2l+1)}\right]}|l,0\rangle|1\rangle + \sqrt{\left[\frac{l(l+2)}{(l+1)(2l+1)}\right]}|l,1\rangle|0\rangle \\ &+\sqrt{\left[\frac{l(l-1)}{2(l+1)(2l+1)}\right]}|l,2\rangle|-1\rangle \approx \frac{1}{2}|l,0\rangle|1\rangle \\ &+\frac{1}{\sqrt{2}}|l,1\rangle|0\rangle + \frac{1}{2}|l,2\rangle|-1\rangle\end{aligned}$$

$$\begin{aligned}|l,l+1,0\rangle = &\sqrt{\left[\frac{l}{2(2l+1)}\right]}|l,-1\rangle|1\rangle + \sqrt{\left[\frac{l+1}{2l+1}\right]}|l,0\rangle|0\rangle \\ &+\sqrt{\left[\frac{l}{2(2l+1)}\right]}|l,1\rangle|-1\rangle \\ \approx &\frac{1}{2}|l,-1\rangle|1\rangle + \frac{1}{\sqrt{2}}|l,0\rangle|0\rangle + \frac{1}{2}|l,1\rangle|-1\rangle\end{aligned}$$

$$\begin{aligned}|l,l+1,-1\rangle = &\sqrt{\left[\frac{l(l-1)}{2(2l+1)(l+1)}\right]}|l,-2\rangle|1\rangle \\ &+\sqrt{\left[\frac{l(l+2)}{(2l+1)(l+1)}\right]}|l,-1\rangle|0\rangle \\ &+\sqrt{\left[\frac{l+2}{2(2l+1)}\right]}|l,0\rangle|-1\rangle \\ \approx &\frac{1}{2}|l,-2\rangle|1\rangle + \frac{1}{\sqrt{2}}|l,-1\rangle|0\rangle + \frac{1}{2}|l,0\rangle|-1\rangle\end{aligned}$$

$$|l,l,1\rangle = -\frac{1}{\sqrt{2}}|l,0\rangle|1\rangle + \frac{1}{\sqrt{[l(l+1)]}}|l,1\rangle|0\rangle + \sqrt{\left[\frac{(l-1)(l+2)}{2l(l+1)}\right]}|l,2\rangle|-1\rangle$$

$$\approx -\frac{1}{\sqrt{2}}|l,0\rangle|1\rangle + \frac{1}{\sqrt{2}}|l,2\rangle|-1\rangle$$

$$|l,l,0\rangle = \frac{1}{\sqrt{2}}|l,1\rangle|-1\rangle - \frac{1}{\sqrt{2}}|l,-1\rangle|1\rangle$$

$$|l,l,-1\rangle = -\sqrt{\left[\frac{(l-1)(l+2)}{2l(l+1)}\right]}|l,-2\rangle|1\rangle - \frac{1}{\sqrt{[l(l+1)]}}|l,-1\rangle|0\rangle + \frac{1}{\sqrt{2}}|l,0\rangle|-1\rangle$$

$$\approx -\frac{1}{\sqrt{2}}|l,-2\rangle|1\rangle + \frac{1}{\sqrt{2}}|l,0\rangle|-1\rangle$$

$$|l,l-1,1\rangle = \sqrt{\left[\frac{l-1}{2(2l+1)}\right]}|l,0\rangle|1\rangle - \sqrt{\left[\frac{l^2-1}{l(2l+1)}\right]}|l,1\rangle|0\rangle + \sqrt{\left[\frac{(l+2)(l+1)}{2l(2l+1)}\right]}|l,2\rangle|-1\rangle$$

$$\approx \frac{1}{2}|l,0\rangle|1\rangle - \frac{1}{\sqrt{2}}|l,1\rangle|0\rangle + \frac{1}{2}|l,2\rangle|-1\rangle$$

$$|l,l-1,0\rangle = \sqrt{\left[\frac{l+1}{2(2l+1)}\right]}|l,-1\rangle|1\rangle - \sqrt{\left[\frac{l}{2l+1}\right]}|l,0\rangle|0\rangle + \sqrt{\left[\frac{l+1}{2(2l+1)}\right]}|l,1\rangle|-1\rangle$$

$$\approx \frac{1}{2}|l,-1\rangle|1\rangle - \frac{1}{\sqrt{2}}|l,0\rangle|0\rangle + \frac{1}{2}|l,1\rangle|-1\rangle$$

$$|l,l-1,-1\rangle = \sqrt{\left[\frac{(l+1)(l+2)}{2l(2l+1)}\right]}|l,-2\rangle|1\rangle - \sqrt{\left[\frac{(l-1)(l+1)}{l(2l+1)}\right]}|l,-1\rangle|0\rangle + \sqrt{\left[\frac{l-1}{2(2l+1)}\right]}|l,0\rangle|-1\rangle$$

$$\approx \frac{1}{2}|l,-2\rangle|1\rangle - \frac{1}{\sqrt{2}}|l,-1\rangle|0\rangle + \frac{1}{2}|l,0\rangle|-1\rangle \qquad (6.2.7)$$

The interaction $\mathscr{V}$ evidently commutes with the total angular momentum, and therefore will have matrix elements only between states with the same values of J and m_J. For each J, however, there are three values of l ($l = J, J+1, J-1$), which may be coupled to one another. $\mathscr{V}$ also commutes with parity, from which it follows that even values of l are never coupled to odd values. This means that $l = J+1$ may be coupled to $J-1$, but $l = J$ is uncoupled to anything else. The matrix elements are independent of m_J because of the scalar nature of the interaction. With the aid of (6.2.3) and (6.2.7), and some more elementary angular momentum theory, it is a straightforward matter to work out the matrix elements of $\mathscr{V}$. They are:

$$\langle J,J,m|\mathscr{V}|J,J,m\rangle = \mu^2/r^3$$

$$\langle J+1,J,m|\mathscr{V}|J+1,J,m\rangle = -\frac{\mu^2}{r^3}\left(\frac{J+2}{2J+1}\right) \approx -\frac{1}{2}\frac{\mu^2}{r^3}$$

$$\langle J+1,J,m|\mathscr{V}|J-1,J,m\rangle = 3\frac{u^2}{r^3}\frac{\sqrt{[J(J+1)]}}{2J+1} \approx \frac{3}{2}\frac{\mu^2}{r^3}$$

$$\langle J-1,J,m|\mathscr{V}|J-1,J,m\rangle = -\frac{\mu^2}{r^3}\left(\frac{J-1}{2J+1}\right) \approx -\frac{1}{2}\frac{\mu^2}{r^3} \quad (6.2.8)$$

In the partial-wave formalism, we decompose the wave function into states with definite J, m_J and solve these separately. The resulting equations are independent of m_J, which will therefore be suppressed in what follows. For each J, m_J, there are three values of l, two of which ($l = J \pm 1$) are coupled to one another. We denote scattering states for each J, l by a bar.

For $l = J$, we can write

$$|\overline{J,J}\rangle = r^{-1}\varphi(r)|J,J\rangle \quad (6.2.9)$$

We then find, using (6.2.8), (6.2.9), that φ obeys

$$-\frac{\hbar}{2m}\varphi'' + \frac{\hbar J(J+1)}{2m}\varphi + \frac{\mu^2}{r^3}\varphi = \frac{p^2}{2m\hbar}\varphi \quad (6.2.10)$$

For $l = J \pm 1$, we must generalize somewhat to take the coupling into account. We can write

$$|\overline{J+1,J}\rangle = r^{-1}\{\xi(r)|J+1,J\rangle + \eta(r)|J-1,J\rangle\} \quad (6.2.11)$$

where we will seek a solution for which $\eta(r)$ goes to zero at infinity. The equation for $|\overline{J-1,J}\rangle$ will be the same, except that $\xi(r)$ is chosen to approach zero. For the present, we anticipate the existence of such solutions, which will be confirmed later on (subsection 6.4).

Combining (6.2.8) with (6.2.11), we find

$$-\frac{\hbar}{2m}\xi'' + \frac{\hbar(J+1)(J+2)}{2mr^2}\xi - \frac{\mu^2}{r^3}\left(\frac{J+2}{2J+1}\right)\xi + 3\frac{\mu^2}{r^3}\frac{\sqrt{[J(J+1)]}}{2J+1}\eta = \frac{p^2}{2m\hbar}\xi$$

$$-\frac{\hbar}{2m}\eta'' + \frac{\hbar J(J-1)}{2mr^2}\eta - \frac{\mu^2}{r^3}\left(\frac{J-1}{2J+1}\right)\eta + 3\frac{\mu^2}{r^3}\frac{\sqrt{[J(J+1)]}}{2J+1}\xi = \frac{p^2}{2m\hbar}\eta \tag{6.2.12}$$

Equations (6.2.10) and (6.2.12) are exact; we now proceed to solve them for the phase shifts near the classical limit.

6.3. *Expansion Near Classical Limit*

1. $l = J$:

Equation (6.2.10) is the same as (6.1.5), with $F(r) = \mu^2/r^3$. We can evaluate the classical limit phase shift directly from (6.1.10):

$$\delta_{(l=J)} = -\frac{\mu^2}{v}\int_b^\infty \frac{dr}{r^2\sqrt{(r^2-b^2)}} = -\frac{\mu^2}{vb^2} = -\frac{\mu^2 p^2}{v\hbar^2 J^2} \tag{6.3.1}$$

We note that, as expected, the only J that contribute appreciably to the cross-section are those satisfying (6.2.6).

2. $l = J \pm 1$:

The treatment of the coupled equations (6.2.12) will be facilitated if it is transformed somewhat. We make the following changes:

(a) The impact parameter $b = \hbar J/p$ is introduced (the difference between J and $J \pm 1$ is negligible here), and the new variable $\rho = r/b$ is substituted.

(b) Certain terms which are of higher order in $\hbar$ and cannot affect the results are dropped. Thus, the limiting form of (6.2.8) is used, and approximations such as $(J+1)(J+2) \cong J^2 + 3J$ are made. It is easily verified that the omitted terms come in at higher order in $\hbar$ than we will need.

(c) We substitute

$$\xi = \exp\left(\frac{i}{\hbar}\lambda\right)$$

$$\eta = \psi\exp\left(\frac{i}{\hbar}\lambda\right) \tag{6.3.2}$$

With all these changes, (6.2.12) and (6.3.2) become

$$\frac{(\lambda')^2}{b^2} - \frac{i\hbar}{b^2}\lambda'' + \frac{p^2}{\rho^2} + \frac{3\hbar p}{b\rho^2} - \frac{m\hbar\mu^2}{b^3\rho^3} + \frac{3m\hbar\mu^2}{b^3\rho^3}\psi = p^2 \tag{6.3.3}$$

$$\frac{(\lambda')^2}{b^2}\psi - \frac{i\hbar}{b^2}\lambda''\psi - \frac{2i\hbar}{b^2}\lambda'\psi' - \frac{\hbar^2}{b^2}\psi'' + \frac{p^2}{\rho^2}\psi - \frac{\hbar p}{b\rho^2}\psi - \frac{m\hbar\mu^2}{b^3\rho^3}\psi + \frac{3m\hbar\mu^2}{b^3\rho^3} = p^2\psi \tag{6.3.4}$$

Differentiations are now with respect to the new variable ρ. We will seek a solution for which ψ goes to zero as ρ goes to infinity.

We now make the expansion in powers of $\hbar$:

$$\lambda = \lambda_0 + \hbar\lambda_1 + \cdots$$

$$\psi = \psi_0 + \hbar\psi_1 + \cdots$$

To zero order in $\hbar$, (6.3.3) becomes

$$\frac{(\lambda_0')^2}{b^2} + \frac{p^2}{b^2} = p^2, \qquad \lambda_0' = bp\sqrt{(1 - 1/\rho^2)} \tag{6.3.5}$$

Equation (6.3.4) in zero order becomes

$$\frac{(\lambda_0')^2}{b^2}\psi_0 + \frac{p^2}{\rho^2}\psi_0 = p^2\psi_0$$

which is automatically satisfied if (6.3.5) is satisfied.

The terms first order in $\hbar$ in (6.3.4) give the equation

$$\frac{2\lambda_0'\lambda_1'}{b^2} - i\frac{\lambda_0''}{b^2} + \frac{3p}{b\rho^2} - \frac{m\mu^2}{b^3\rho^3} + \frac{3m\mu^2}{b^3\rho^3}\psi_0 = 0 \tag{6.3.6}$$

As in Section 6.1, the phase *shift* is given by:

$$\delta = \mathrm{Re}\,[\lambda_1(\infty) - \lambda_1(\infty)|\mu^2 = 0]$$

so we have, from (6.3.5) and (6.3.6),

$$\delta(l = J + 1) = \frac{m\mu^2}{2b^2p}\int_1^\infty \frac{(1 - 3\,\mathrm{Re}\,\psi_0)\,d\rho}{\rho^2\sqrt{(\rho^2 - 1)}} = \frac{\mu^2}{2vb^2}(1 - 3Q) \tag{6.3.7}$$

where

$$Q = \mathrm{Re}\int_1^\infty \frac{\psi_0(\rho)\,d\rho}{\rho^2\sqrt{(\rho^2 - 1)}} \tag{6.3.8}$$

To get an equation satisfied by ψ_0, we must consider the first-order terms in (6.3.4). These give the equation

$$\frac{(\lambda_0')^2}{b^2}\psi_1 + \frac{2\lambda_0'\lambda_1'}{b^2}\psi_0 - \frac{i}{b^2}\lambda_0''\psi_0 - \frac{2i}{b^2}\lambda_0'\psi_0' + \frac{p^2}{b^2}\psi_1 - \frac{p}{b\rho^2}\psi_0 - \frac{m\mu^2}{b^3\rho^3}\psi_0 + \frac{3m\mu^2}{b^3\rho^3} = p^2\psi_1 \tag{6.3.9}$$

The terms in (6.3.9) containing ψ_1 drop out because of (6.3.5). Terms involving λ_0, λ_1 may be eliminated by substituting (6.3.5), (6.3.6). When this is done, one finds the following nonlinear equation for ψ_0:

$$-\frac{3m\mu^2}{b^3\rho^3}\psi_0^2 - \frac{4p}{b\rho^2}\psi_0 - \frac{2ip}{b\rho}\sqrt{(\rho^2-1)}\,\psi_0' + \frac{3m\mu^2}{b^3\rho^3} = 0 \tag{6.3.10}$$

Because of its nonlinear character, we will not be able to find the solution to (6.3.10). We will, however, be able to discover enough properties of the solution to enable us to evaluate Q, which is all we need.

6.4. *Evaluation of Q*

In (6.3.10), let us make the change of variables $y = (\rho^2 - 1)^{1/2}$, and the substitution

$$\psi_0 = \rho\chi$$

With these changes, (6.3.10) becomes

$$\chi^2 + \Gamma(2+iy)\chi + i\Gamma(y^2+1)\chi' - \frac{1}{y^2+1} = 0 \tag{6.4.1}$$

where

$$\Gamma = \frac{2pb^2}{3m\mu^2}$$

In terms of the new variables, (6.3.8) becomes

$$Q = \mathrm{Re}\int_0^\infty \frac{\chi(y)\,dy}{y^2+1} \tag{6.4.2}$$

Since we want ψ_0 to vanish at infinity, it is necessary to examine (6.4.1) for large values of y, to see whether this is possible. For large y, therefore, we try a solution $\chi = ay^{-n}$, and take only the leading contributions from each term in (6.4.1). We find

$$a^2y^{-2n} + i\Gamma a y^{-n+1} - in\Gamma a y^{-n+1} - y^{-2} = 0$$

which has to be satisfied only to the lowest negative power of y appearing in it. We see that this can be satisfied for $n = 3$ or 1. (If $n = 1$, the two middle terms are the leading ones; if $n = 3$, all the terms except the first must be kept.) We must choose $n = 3$, since we want $\psi_0 = \rho\chi$ to vanish at infinity. With this choice, requiring the term in y^{-2} in (6.4.1) to vanish leads to the result

$$a = i/2\Gamma$$

so the asymptotic behavior of χ is given by

$$\chi \approx \frac{i}{2\Gamma y^3}, \qquad y \to \infty \tag{6.4.3}$$

for the solution which is acceptable to us.

Equation (6.4.1) is of the Riccati type.† It may be transformed by means of the substitution

$$\chi(y) = i\Gamma(y^2 + 1)\frac{f'}{f} \tag{6.4.4}$$

By inserting (6.4.4) into (6.4.1) and performing some simple manipulations, we find

$$f'' + \frac{3y - 2i}{y^2 + 1}f' + \frac{1}{\Gamma^2(y^2 + 1)^3}f = 0 \tag{6.4.5}$$

Insertion of (6.4.4) into (6.4.2) gives the result

$$Q = \operatorname{Re} i\Gamma \int_0^\infty \frac{f'}{f}\,dy = -\Gamma[\operatorname{Im} \ln f]_0^\infty \tag{6.4.6}$$

Thus, we only need to find the change in phase of f between zero and infinity.

Equation (6.4.5) has two linearly independent solutions. We must choose the one which leads to the correct asymptotic behavior for χ. Substituting $f \approx y^n$ into (6.4.6), and taking the leading terms for large y, we find $n = 0, -2$. According to (6.4.3) and (6.4.4), we should have $f'/f \sim y^{-5}$ for large y, so clearly $n = -2$ is unacceptable. Choosing $n = 0$, we can now calculate the next term. Write

$$f = 1 + ay^{-\nu} + \cdots$$

† See, for example, Murphy, G. M. (1960). *Ordinary Differential Equations and their Solutions*, pp. 15–20. D. Van Nostrand, Princeton, N.J.

One then substitutes this into (6.4.5) and takes leading terms, with the result

$$\nu(\nu-2)\,ay^{-\nu-2}+\frac{1}{\Gamma^2}y^{-6}=0$$

One solution is $\nu=2$, with the last term dropping out in this case. This is easily seen not to give the right asymptotic behavior. The other solution is

$$\nu=4, \qquad a=-(8\Gamma^2)^{-1}$$

which is the acceptable one. For large y, therefore, we have

$$f=1-\frac{1}{8\Gamma^2}y^{-4}+\cdots \tag{6.4.7}$$

Substituting (6.4.7) into (6.4.4), one finds that (6.4.3) is indeed satisfied asymptotically. f is, of course, determined only up to a multiplicative constant, which drops out when χ is evaluated by (6.4.4). We have fixed this for convenience by requiring the constant term in the asymptotic expansion to be unity.

Combining (6.4.7) with (6.4.6), we find

$$Q=\Gamma[\operatorname{Im}\ln f(0)] \tag{6.4.8}$$

where f must now be the solution which satisfies (6.4.7) asymptotically.

We now notice that if $f(y)$ is a solution of (6.4.5), so is $f^*(-y)$. Also, if $f(y)$, $g(y)$ are any two solutions, one easily deduces the Wronskian equation

$$W'=\left(\frac{2i-3y}{y^2+1}\right)W$$

where $W=gf'-fg'$. The solution is

$$W=\frac{K}{(y-i)^{1/2}(y+i)^{5/2}} \tag{6.4.9}$$

where K is a constant. Now, let $f(y)$ be the solution satisfying (6.4.7), $g(y)=f^*(-y)$. From (6.4.8), it is easily seen that for large y, $W=0(y^{-5})$. According to (6.4.9), however, W must behave asymptotically as Ky^{-3}. It follows that $K=0$, $W=0$ everywhere.

$W=0$ implies that $f^*(-y)$ is just a constant times $f(y)$, and it is clear from (6.4.7) that this constant must be unity. We conclude that

$$f^*(-y)=f(y) \tag{6.4.10}$$

(It is clear that the continuation to negative y is permissible, since (6.4.5) has no singular points on the real axis.) Also, one sees from (6.4.4) that the solution with $f(0)=0$ leads to unacceptable behavior

of χ at $y = 0$, and is therefore not of interest. This solution would lead to infinite cross-sections.†

It follows from (6.4.10) and the fact that $f(0) \neq 0$ that $\mathrm{Im}\, f$ is an odd function of y, hence $\mathrm{Im}\, f(0) = 0$, $\mathrm{Re}\, f(0) \neq 0$. Therefore, $\mathrm{Im} \ln f(0) = n\pi$, where n is some integer, positive or negative. Hence, from (6.4.8),

$$Q = \Gamma n\pi \tag{6.4.11}$$

Combining (6.4.11) with (6.3.7) and (6.4.1), we find

$$\delta(l = J + 1) = \frac{\mu^2}{2vb^2} - n\pi \tag{6.4.12}$$

All the properties of the phase shift which are of interest ($\sin^2\delta$, $32i\delta$) are independent of n, so we can take $n = 0$. The calculation for $l = J - 1$ is exactly similar, and yields the same result.

The final result, therefore, is just the same as if we had completely ignored the coupling between the different l-values. After the fact, this result seems rather reasonable. This method has been shown to be equivalent to the classical path method; in that method, the impact parameter (or orbital angular momentum) is treated as a fixed c-number, and one cannot even express the idea of a transition (real or even virtual) in which the value of this c-number changes. The coupling between different l-values, therefore, is a concept foreign to the idea of the classical path approximation, so its effects should be expected to disappear.

We now have all the phase shifts that we need. All that remains is to put them together to get the scattering matrix and cross sections.

6.5. *Results*: *Comparison with Other Theories*

Equations (6.3.1) and (6.4.12) provide us with all the information we need to calculate the scattering matrix. The phase shift for $l = J - 1$ is the same as (6.4.12), and the results for the antisymmetric linear combinations are obtained by replacing μ^2 with $-\mu^2$.

† The solution with $f(0) = 0$ varies linearly with y for small y, so to satisfy (6.4.10) it must obey $f(y) \approx \sigma iy$, $y \to 0$, where σ is real. With this solution, (6.4.12) would become

$$\delta = \frac{\mu^2}{2vb^2} - (n + \tfrac{1}{2})\,\pi$$

which has as a consequence $\sin^2\delta \to 1$, as $b \to \infty$. This would cause the expression for the cross-section to diverge.

Using (6.1.12), (6.3.1), (6.4.12), we find

$$\langle J,J,m(\pm)|\mathscr{S}|J,J,m(\pm)\rangle = \exp(\mp 2i\zeta)$$
$$\langle J+1,J,m(\pm)|\mathscr{S}|J+1,J,m(\pm)\rangle = \langle J-1,J,m(\pm)|\mathscr{S}|J-1,J,m(\pm)\rangle = \exp(\pm i\zeta) \tag{6.5.1}$$

where $\zeta = \mu^2/vb^2$, $b = \hbar J/p$, and other matrix elements are zero.

Matrix elements involving initial states such as $|l,0\rangle|1\rangle$ are obtained by taking the appropriate linear combinations. For example, using (6.5.1) and the limiting form of (6.2.7), which is adequate to the order of approximation we are considering, we find

$$\begin{aligned}\mathscr{S}|l,0\rangle|1(+)\rangle &= \mathscr{S}\{\tfrac{1}{2}|l,l+1,1(+)\rangle - \sqrt{(\tfrac{1}{2})}|l,l,1(+)\rangle \\ &\quad +\tfrac{1}{2}|l,l-1,1(+)\rangle\} \\ &= \tfrac{1}{2}\exp(i\zeta)|l,l+1,1(+)\rangle - \sqrt{(\tfrac{1}{2})}\exp(-2i\zeta)|l,l,1(+)\rangle \\ &\quad +\tfrac{1}{2}\exp(i\zeta)|l,l-1,1(+)\rangle \\ &= \tfrac{1}{2}[\exp(i\zeta)+\exp(-2i\zeta)]\{|l,0\rangle|1(+)\rangle + |l,2\rangle|-1(+)\rangle\}\end{aligned}$$

etc. States with the excitation localized on A or B are obtained by taking linear combinations of symmetric and antisymmetric states.

When the matrix elements are calculated for these direct product states, it is found that they never connect states of different l, and also that they depend only on l (or b) and the initial and final values of m_S. Thus, the amplitude for a transition in which m_S changes from 1 to -1 is the same whether one treats m_l as going from zero to 2 or from -2 to zero. This is necessary to obtain correspondence with the classical path method, in which m_l does not appear. We can therefore suppress all indices except the ones telling which atom is excited and the value of m_S. The resulting matrix elements are:

$$\begin{aligned}\langle A,0|\mathscr{S}|A,0\rangle &= \langle B,0|\mathscr{S}|B,0\rangle = \cos\zeta \\ \langle A,0|\mathscr{S}|B,0\rangle &= \langle B,0|\mathscr{S}|A,0\rangle = i\sin\zeta \\ \langle A,1|\mathscr{S}|A,1\rangle &= \langle B,1|\mathscr{S}|B,1\rangle = \langle A,-1|\mathscr{S}|A,-1\rangle \\ &= \langle B,-1|\mathscr{S}|B,-1\rangle = \cos(\zeta/2)\cos(3\zeta/2) \\ \langle A,1|\mathscr{S}|A,-1\rangle &= \langle A,-1|\mathscr{S}|A,1\rangle = \langle B,1|\mathscr{S}|B,-1\rangle \\ &= \langle B,-1|\mathscr{S}|B,1\rangle = \sin(\zeta/2)\sin(3\zeta/2) \\ \langle A,1|\mathscr{S}|B,1\rangle &= \langle A,-1|\mathscr{S}|B,-1\rangle = \langle B,1|\mathscr{S}|A,1\rangle \\ &= \langle B,-1|\mathscr{S}|A,-1\rangle = -i\sin(\zeta/2)\cos(3\zeta/2) \\ \langle A,1|\mathscr{S}|B,-1\rangle &= \langle A,-1|\mathscr{S}|B,1\rangle = \langle B,1|\mathscr{S}|A,-1\rangle \\ &= \langle B,-1|\mathscr{S}|A,1\rangle = i\cos(\zeta/2)\sin(3\zeta/2)\end{aligned} \tag{6.5.2}$$

All others are zero.

The $\mathscr{S}$-matrix assumes a simpler form if we define the polarized states

$$|A_z\rangle = |A,0\rangle$$
$$|A_x\rangle = \sqrt{(\tfrac{1}{2})}\,(|A,1\rangle + |A,-1\rangle)$$
$$|A_y\rangle = \sqrt{(\tfrac{1}{2})}\,(|A,1\rangle - |A,-1\rangle) \qquad (6.5.3)$$

It is seen that the x-polarization is invariant under reflections through planes containing the z-axis, while y changes sign. Thus, the x-direction for a particular path may be thought of as pointing directly outward along the interatomic radius at the point of closest approach, while y is chosen in such a way as to form a right-handed coordinate system

TABLE 1. $\mathscr{S}$-matrix elements as obtained by different methods

Element	Present work	Byron & Foley (1964)
$\langle A_z\|\mathscr{S}\|A_z\rangle$	$\cos\zeta$	1
$\langle A_z\|\mathscr{S}\|B_z\rangle$	$i\sin\zeta$	0
$\langle A_x\|\mathscr{S}\|A_x\rangle$	$\cos\zeta$	$\cos 2\zeta$
$\langle A_x\|\mathscr{S}\|B_x\rangle$	$i\sin\zeta$	$i\sin 2\zeta$
$\langle A_y\|\mathscr{S}\|A_y\rangle$	$\cos 2\zeta$	$\cos 2\zeta$
$\langle A_y\|\mathscr{S}\|B_y\rangle$	$-i\sin 2\zeta$	$-i\sin 2\zeta$

Elements obtained by exchanging A and B are the same as those listed. All others are zero. $\zeta = \mu^2/vb^2$.

with x and z. The results for this representation are given in Table 1. For comparison, we also list the results that would be obtained using the method of Byron & Foley (1964), which consists in neglecting the time-ordering in equation (4.4.2). We note that the two methods give the same result for the y-polarization; this is because it is not coupled to the other directions (r_y always being zero), so the interaction becomes simply a number, not a matrix, for this polarization, making the order of factors irrelevant.

Cross-sections may be evaluated either by means of the phase shift formula or by using the information in Table 1 and the formula

$$\sigma_{j\to k} = 2\pi \int_0^\infty b\,|\mathscr{S}_{kj}(b) - \delta_{kj}|^2\,db$$

[compare equation (6.1.3)]. The results are summarized in Table 2. We also list the results that would follow from the method of Byron & Foley (1964) and those which were obtained numerically by Watanabe (1965a, b). The method of Byron and Foley is seen to give the correct result for the average total cross section, but not for the individual cross sections. Watanabe's result for the average total

TABLE 2. Cross-sections calculated by different methods

k	Present work	Byron & Foley (1964)	Watanabe (1965a, b)
$A_z \to A_z$	1/2	0	†
$A_z \to B_z$	1/2	0	0·137
$A_z \to A_x$	0	0	0·192
$A_z \to B_x$	0	0	0·179
$A_y \to A_y$	1	1	†
$A_y \to B_y$	1	1	1·000
$A_x \to A_x$	1/2	1	†
$A_x \to B_x$	1/2	1	0·656
$A_x \to A_z$	0	0	0·192
$A_x \to B_z$	0	0	0·178
Average Total	4/3	4/3	1·44†

† Watanabe did not calculate cross-sections for scattering without change in internal state. The total average cross section is calculated by assuming that it is twice that for excitation transfer.

For each process, the cross section $\sigma = k\pi^2\mu^2/v$. Cross-sections for initial states with B excited are obtained by interchanging A and B. Others are zero by all three methods.

cross section differs by somewhat less than 10%. From equation (4.4.6) and Table 2, we conclude that

$$k_i = 4/3$$

It is perhaps advisable to discuss briefly the probable reasons for the discrepancy between Watanabe's results and ours. His method consists in expanding the time-ordered exponential (4.4.2) in a power series in μ^2, performing the integrations (up to the fiftieth order) numerically on a computer, then squaring the resulting $\mathscr{S}$-matrix

elements and integrating them to obtain the cross sections. A difficulty with this method is that the integral diverges badly at the origin (as may be seen by expanding our $\mathscr{S}$-matrix elements in powers of μ^2), so a somewhat arbitrary cutoff procedure has to be used. The uncertainty thus introduced is probably sufficient to account for most of the discrepancies. It still seems rather strange at first glance that we obtain exactly zero cross sections for processes in which the polarization changes from x to z or vice versa, while Watanabe obtains nonzero results, comparable in magnitude to the cross-sections for other processes. If one checks back through the calculation, one finds that the vanishing of this cross-section is due to the result (6.4.11), which embodies the fact that the phase of the function f, obeying equation (6.4.5), changes by an integer times π when y goes from zero to infinity. It is evident from (6.4.5), however, that the phase of f does change in this process (e.g., it is not always zero), and that its detailed behavior is likely to be quite complicated. It is not too surprising, therefore, that a numerical calculation fails to give the result that the overall phase change is exactly $n\pi$.

7. *Many-Body Corrections*

In the static limit, it has already been shown (Reck *et al.*, 1965) that the corrections for three-body processes are of order of magnitude $\mathscr{N}\mu^2/\lambda$ relative to the two-body terms, with higher-order corrections involving successively higher powers of $\mathscr{N}\mu^2/\lambda$. Hence, the criterion for use of the two-body approximation in this limit is

$$\lambda \gg \mathscr{N}\mu^2 \tag{7.1}$$

The approximation is always good on the wings of the line, therefore, but never for the center. Since, according to equation (2.2), the line shape must be averaged over velocities, the many-body effects will fail to be noticeable if

$$D \gg \mathscr{N}\mu^2 \tag{7.2}$$

where D is the Doppler width. In the static limit, therefore, one may always use the two-body approximation for the portion of the line satisfying (7.1). If (7.2) is satisfied, it may be used for the entire line without appreciable error.

We now consider many-body corrections in the impact limit, i.e., in the limit where the two-body U operator is given accurately by the theory of Section 4.4. We will content ourselves with estimating the order of magnitude of these processes, and will therefore ignore polarization indices. Equations (4.1.1) and (4.1.2) may be thought of

as representing a series of independent collisions, in each of which the excitation remains on atom A. In shorthand notation, they say that

$$\langle A|U|A\rangle = \prod_{D\neq A} \langle A|U_{AD}|A\rangle$$

The next higher-order effect is that due to processes in which the excitation is transferred from A to another atom B, from there to C, and back to A again. The correction for this effect may be written

$$\delta\langle A|U|A\rangle = \sum_{B,C\neq A} \langle A|U_{AB}|B\rangle\langle B|U_{BC}|C\rangle\langle C|U_{CA}|A\rangle \times \times \prod_{D\neq A,B,C} \langle A|U_{AD}|A\rangle \tag{7.3}$$

which must, of course, be averaged over configuration space. When this average is carried out, the product over D in (7.3) just gives $\exp(-1/2\mathcal{N}\sigma vt)$ in the impact limit as before. The rest of (7.3), when averaged, contains the following factors:

N^2 (from summing over B and C);

V^{-2} (normalization for volume average);

σvt (twice, from integrating U_{AB} over r_B and U_{BC} over r_C and using the impact limit for each U);

$\sigma/(vt)^2$ (solid angle factor from U_{CA}. May be thought of as probability that C, having collided with B, will be 'aimed right' to collide with A after travelling a distance $\sim vt$.).

Putting all this together, we find

$$\delta\langle A|U|A\rangle \sim \mathcal{N}^2\sigma^3\langle A|U|A\rangle \tag{7.4}$$

This correction will be small compared with the two-body term if

$$\mathcal{N}^2\sigma^3 \ll 1$$

But this is immediately seen to be the same as (4.4.11). Thus, the criterion for use of the impact limit for the main part of the line within the two-body approximation is the same as that for neglect of many-body processes in this limit.

To sum up, then, if the classical path approximation is assumed to be valid, one may use the static two-body approximation if the conditions

$$\begin{aligned} \lambda &\gg \mathcal{N}\mu^2 \\ \lambda &\gg v/\sqrt{\sigma} \sim \sqrt{(v)}/\mu \end{aligned} \tag{7.5}$$

are satisfied. The criteria for use of the two-body impact approximation are

$$\begin{aligned} \lambda &\ll \sqrt{(v)}/\mu \\ \mathcal{N}\mu^2 &\ll \sqrt{(v)}/\mu \end{aligned} \tag{7.6}$$

where v, of course, is always understood to be some appropriate average velocity.

8. *Quantum Corrections*

To obtain the lowest-order quantum corrections to the classical path approximation, one must solve equation (3.9). We notice that the first two terms on the right-hand side of (3.9) are trivial and uninteresting: the first is a constant which could be absorbed into λ, while the second is simply a correction to $\mathbf{v}_A$, and could be included in the second term of (3.8). Only the last term is really important, so we can find the true quantum correction by solving

$$\left(\lambda + i\sum_D \mathbf{v}_D \cdot \nabla_D - \mathscr{V}\right)\mathscr{R}_1 = -\frac{1}{2m}\sum_D \nabla_D{}^2 \mathscr{R}_0 \tag{8.1}$$

This is easily solved formally by the methods of Section 3, equations (3.23) and (3.24). The result is

$$\mathscr{R}_1(\eta,\tau) = -\frac{1}{2m}\int_0^\infty\int_0^\infty U_\eta(\tau|\tau-t)\sum_D \nabla_D{}^2\, U_\eta(\tau-t|\tau-t-t')$$
$$\times \exp[i\lambda(t+t')]\,dt\,dt' \tag{8.2}$$

Since this must eventually be averaged over configuration space, it is clear the final result will not be affected if the origin is shifted by t. If we do this, and go back to the $\mathbf{r}$ representation, we find for the correction to the resolvent

$$R_1 = -\frac{1}{2mV^N}\int d^{3N}r\int_0^\infty\int_0^\infty U(\mathbf{r}+\mathbf{v}t|\mathbf{r})\sum_D \nabla_D{}^2\, U(\mathbf{r}|\mathbf{r}-\mathbf{v}t')$$
$$\times \exp[i\lambda(t+t')]\,dt\,dt' \tag{8.3}$$

If we can make the two-body approximation, then each U is a product of independent U_{AD} operators for the matrix element in which we are interested. In this case, each $\nabla_D{}^2$ operates only on the factor U_{AD}, and (8.3) can be rewritten

$$R_1 = -\frac{1}{2mV^N}\int d^{3N}r\int_0^\infty\int_0^\infty \sum_{D\neq A}\{U_{AD}(\mathbf{r}_{AD}+\mathbf{v}_{AD}t|\mathbf{r}_{AD})\nabla_D{}^2 \times$$
$$\times\, U_{AD}(\mathbf{r}_{AD}|\mathbf{r}_{AD}-\mathbf{v}_{AD}t')\}\prod_{C\neq A,D} U_{AC}(\mathbf{r}_{AC}+\mathbf{v}_{AC}t|\mathbf{r}_{AC}$$
$$-\,\mathbf{v}_{AC}t')\exp[i\lambda(t+t')]\,dt\,dt' \tag{8.4}$$

In (8.4) it is understood that matrix elements $\langle A|U|A\rangle$, etc., are to be taken, i.e., (8.4) holds only for these matrix elements, not as an operator equation. We will content ourselves with estimating the order of magnitude of (8.4) in the two limiting cases, static and impact.

First, we notice that the product over C in (8.4), after integration over $\mathbf{r}$, behaves just as in Section 4 and gives the result

$$\exp\left[-\tfrac{1}{2}k\pi^2\mathcal{N}\mu^2(t+t')\right]$$

where k is either k_i or k_s, as the case may be. Therefore, we can rewrite (8.4) as

$$\begin{aligned} R_1 &= -\frac{1}{2m}\mathcal{N}\int d^3r \int_0^\infty\int_0^\infty U(\mathbf{r}+\mathbf{v}t|\mathbf{r})\,\nabla^2\,U(\mathbf{r}|\mathbf{r}-\mathbf{v}t')\times \\ &\quad\times\exp\left[iA(t+t')\right]dt\,dt' \\ &= \frac{1}{2m}\mathcal{N}\int d^3r\int_0^\infty\int_0^\infty \{\nabla U(\mathbf{r}+\mathbf{v}t|\mathbf{r})\}.\{\nabla U(\mathbf{r}|\mathbf{r}-\mathbf{v}t')\}\times \\ &\quad\times\exp\left[iA(t+t')\right]dt\,dt' \end{aligned} \tag{8.5}$$

where $A=\lambda+(1/2)ik\pi^2\mathcal{N}\mu^2$, and the last equality has been obtained by integration by parts. The sum over D has been replaced by a factor of N, and it is understood that one must eventually average over $\mathbf{v}$.

Now, in the static limit, we have (neglecting angles and polarization, since we are only interested in order of magnitude)

$$\begin{aligned} U(\mathbf{r}|\mathbf{r}-\mathbf{v}t) &= \exp\left[-i\mathcal{V}(\mathbf{r})\,t\right] \\ \nabla U &\sim 3i\hat{r}\frac{\mu^2}{r^4}t\exp\left(-i\frac{\mu^2}{r^3}t\right) \end{aligned} \tag{8.6}$$

where $\hat{r}$ is a unit vector in the direction of $\mathbf{r}$. If (8.6) is inserted into (8.5), one finds

$$R_1 \sim -\frac{1}{2m}\mathcal{N}\int d^3r\int_0^\infty\int_0^\infty \frac{\mu^4}{r^8}tt'\exp i\left(A-\frac{\mu^2}{r^3}\right)(t+t')\,dt\,dt'$$

By performing the t, t' integrations, and making the change of variables $\mathbf{r}=(\mu^2/A)^{1/3}\boldsymbol{\rho}$, we obtain

$$\begin{aligned} \hbar R_1 &\sim -\frac{\hbar\mathcal{N}\mu^{2/3}}{2mA^{7/3}}B \\ B &= \int\frac{d^3\rho}{\rho^8(1-1/\rho^3)} \end{aligned} \tag{8.7}$$

We can think of this as a correction to the width by writing

$$R = \frac{1}{\Lambda + \Delta} \approx \frac{1}{\Lambda} - \frac{\Delta}{\Lambda^2} + \cdots \tag{8.8}$$

From (8.7) and (8.8), we find

$$\Lambda_{qs} \sim \frac{\hbar \mathcal{N} \mu^{2/3}}{2m\Lambda^{1/3}} \tag{8.9}$$

where the subscript qs indicates quantum correction on static limit. It is seen that the correction is always small if one goes sufficiently far out on the wings of the line.

To treat the impact case, we choose our z-axis in the direction of v, and treat only the contribution of $\partial/\partial z$ in (8.5). The reader may verify that the result for the other directions is of the same order of magnitude as what we will obtain for the $\partial/\partial z$ contribution. From the way U is defined, it is clear that

$$\frac{\partial}{\partial z} U(\mathbf{r} + \mathbf{v}t|\mathbf{r}) = -\frac{i}{v}[\mathscr{V}(\mathbf{r} + \mathbf{v}t)\, U - U\mathscr{V}(\mathbf{r})]$$

from which we obtain

$$\begin{aligned}
&\left\{\frac{\partial}{\partial z} U(\mathbf{r} + \mathbf{v}t|\mathbf{r})\right\} \left\{\frac{\partial}{\partial z} U(\mathbf{r}|\mathbf{r} - \mathbf{v}t')\right\} \\
&\quad = \frac{1}{v^2}\{\mathscr{V}(\mathbf{r} + \mathbf{v}t)\, U(\mathbf{r} + \mathbf{v}t|\mathbf{r}) - U(\mathbf{r} + \mathbf{v}t|\mathbf{r})\, \mathscr{V}(\mathbf{r})\} \times \\
&\qquad \times \{\mathscr{V}(\mathbf{r})\, U(\mathbf{r}|\mathbf{r} - \mathbf{v}t') - U(\mathbf{r}|\mathbf{r} - \mathbf{v}t')\, \mathscr{V}(\mathbf{r} - \mathbf{v}t')\} \\
&\quad \approx \frac{1}{v^2} U(\mathbf{r} + \mathbf{v}t|\mathbf{r})\, \mathscr{V}^2(\mathbf{r})\, U(\mathbf{r}|\mathbf{r} - \mathbf{v}t')
\end{aligned} \tag{8.10}$$

where the last approximate equality follows from the fact that, in the impact limit with vt large, the interaction $\mathscr{V}$ must be small at at least two of the positions $\mathbf{r}$, $\mathbf{r} + \mathbf{v}t$, $\mathbf{r} - \mathbf{v}t'$. The part that is kept is the only part of the whole expression which can ever be very large. To estimate the order of magnitude of (8.10), we first move $\mathscr{V}^2$ to the left, neglecting the commutator, and obtain

$$\frac{1}{v^2} \mathscr{V}^2(\mathbf{r})\, U(\mathbf{r} + \mathbf{v}t|\mathbf{r} - \mathbf{v}t') \approx \frac{1}{v^2} \mathscr{V}^2(\mathbf{r})\, \mathscr{S}(x, y) \tag{8.11}$$

where we have used the fact that $U = \mathscr{S}$ wherever $\mathscr{V}^2(r)$ is appreciable. Putting (8.11) into (8.5), and doing the t, t' integrations, we find

$$R_1 \sim \frac{\mathcal{N}}{2mv^2\Lambda^2} \int d^3 r \mathscr{V}^2(\mathbf{r})\, \mathscr{S}(x, y) \tag{8.12}$$

We now note that $\mathscr{V} \sim \mu^2/r^3$, and $\mathscr{S} = \mathscr{S}(\mu^2/vb^2)$, and make the change of variables $\mathbf{r} = (\mu/v^{1/2})\boldsymbol{\rho}$. This leads to the result

$$\hbar R_1 \sim -\frac{\hbar \mathscr{N} \mu}{2m\sqrt{(v)}\,\Lambda^2} C$$

$$C = \int \frac{\mathscr{S}(1/\beta^2)\, d^3\rho}{\rho^6} \tag{8.13}$$

$$\beta^2 = {\rho_x}^2 + {\rho_y}^2$$

As a correction to the width, as in (8.9), this becomes

$$\Delta_{qi} \sim \frac{\hbar \mathscr{N} \mu}{m\sqrt{v}} \tag{8.14}$$

This correction is seen to be independent of λ, but to depend on v. Since it is seen to be real, it would just give a shift of the line proportional to $\mathscr{N}$ if v were constant. Since v must be averaged over, this term will lead to an effective broadening of the line.

9. *Comparison with Experiment*

During the 1940's, several experimental studies were carried out on pressure broadening of the alkali metal doublets (Chen, 1940; Watanabe, 1941; Gregory, 1942). In all these studies, only the wings of the line were observed, and the width deduced with the aid of the assumption that the line was Lorentzian. Since only the wings are involved, the static two-body approximation should apply. In agreement with theory, the width is observed to vary linearly with the density. In order to compare the coefficient with experiment, the constant k_s was evaluated for the two components of the doublet in Reck *et al.* (1965). The result is

$$k(3/2) = \frac{7 + 2\sqrt{7}}{6} = 2{\cdot}05$$

$$k(1/2) = 8/3 = 2{\cdot}67$$

The broadening is proportional to the oscillator strength times k, and is therefore expected to be greater for the 3/2 component. These theoretical values are compared with experiment in Table 3. It is essentially the same as those given by Reck *et al.* (1965, Table 1), except that the results are expressed in terms of k, a minor error has been corrected, and the oscillator strength for sodium has been corrected to agree with the experimental results of Kibble *et al.* (1967). For rubidium and cesium, it has been assumed that the total oscillator

strength of the doublet is unity. This is supported by some of the experimental data (Kuhn, 1962), but not all (Stone, 1962), so it must be concluded that these oscillator strengths are not known very accurately. Since the experimental value of k varies inversely as the *square* of the assumed oscillator strength, it follows that there is some uncertainty in comparing all quantities except the ratio of the two k-values. It is seen that the agreement is satisfactory, in view of these uncertainties.

The reflection experiments of Lauriston & Welsh (1951) have also been discussed (Reck *et al.*, 1965). These were performed on alkali metal vapors at temperatures in the vicinity of 1000°K, and pressures

TABLE 3. Comparison of theory with experiment for broadening in wings of alkali metal doublets

Quantity	$k(3/2)$	$k(1/2)$	$k(3/2)/k(1/2)$	Reference
Theory:	2·05	2·67	0·768	Present work and Reck *et al.* (1965)
Experiment:				
Na	$2{\cdot}3 \pm 0{\cdot}3$	$4{\cdot}1 \pm 0{\cdot}5$	$0{\cdot}58 \pm 0{\cdot}05$	Watanabe (1941)
Rb	$2{\cdot}2 \pm 0{\cdot}6$	$2{\cdot}7 \pm 0{\cdot}9$	$0{\cdot}83 \pm 0{\cdot}07$	Chen (1940)
Cs	$2{\cdot}4 \pm 0{\cdot}3$	$2{\cdot}7 \pm 0{\cdot}4$	$0{\cdot}9 \pm 0{\cdot}2$	Gregory (1942)

in some cases approaching one atmosphere. Neither limiting approximation is really applicable here, since $\mathcal{N}\mu^2$ and $v/\sqrt{\sigma}$ turn out to be of the same order of magnitude. Since (7.6) is not satisfied, many-body effects are expected to be important, and in fact it is observed that the width varies as the square root of the density rather than linearly. The theory developed by Reck *et al.* (1965), in which a restricted class of the many-body interactions is summed in the static approximation, gives qualitatively correct results: the square root dependence is explained, and the right order of magnitude is obtained for the coefficient. These results, therefore, are at least qualitatively explained by the present theory.

Studies of the emission spectrum of Helium have been carried out by Kuhn & Vaughan (1964), and by Vaughan (1966). They measured the shape of the emission line $3\,^1S \rightarrow 2\,^1P$ (7281 Å). The shape was fitted to a Voigt profile (which it fits very well), and, the $3\,^1S$ level

being very narrow, the Lorentzian width was interpreted as entirely due to the broadening of the $2\,^1P$ level, i.e., of the line $2\,^1P \rightarrow 1\,^1S$ (584 Å). The experiments were done at temperatures ranging from 11°K (Kuhn & Vaughan, 1964) to 280°K (Vaughan, 1966). The highest densities were of the order of 10^{18} atoms per cubic centimetre. The oscillator strength for this transition has been accurately calculated by Schiff & Pekeris (1964), and has the value 0·276, from which one calculates

$$\mu^2 = 1{\cdot}08 \times 10^{-9}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$$

Equation (4.4.11) is very well satisfied under the conditions of these experiments, so one expects the two-body impact approximation to be valid. The quantum corrections, however, are not negligible. Using equation (8.14), one finds

$$\frac{\Delta_{qi}}{\mathcal{N}\mu^2} \sim \frac{\hbar}{\mu m \sqrt{v}} = 0{\cdot}05$$

where v has been taken as the root-mean-square velocity at 11°K. The quantum effects, therefore, should further broaden the line (by several percent of the impact-theory broadening), and cause it to deviate somewhat from a true Voigt profile. The additional broadening is still proportional to the density. If one fits the result to Voigt profiles, therefore, one would expect the Lorentzian width to vary linearly with the density, but with an observed k-value of the order of several percent larger than the impact result $k_i = 4/3$. Experimentally, Kuhn & Vaughan (1964) found $k = 1{\cdot}61 \pm 0{\cdot}11$. The result of Vaughan (1966), believed to be more accurate, is $k = 1{\cdot}44 \pm 0{\cdot}09$. It is seen that there is reasonable agreement, in that the quantum effects are of the right order of magnitude to account for the discrepancy between the experimental k and the result of impact theory. The fact that Vaughan's experimental k agrees with that calculated by Watanabe (1965a, b) and Omont (1966) is evidently fortuitous. It is also possible, though it seems doubtful, that quantum effects provide part of the explanation for the observed anomalous extrapolated width at zero density observed in these experiments. To test the theory more accurately, one would have to try to fit the data to a curve satisfying (8.8) and (8.14) folded into a Gaussian, rather than a strict Voigt profile. A further problem in interpreting these experiments is that there is reason to believe (Lyon, private communication) that there are terms contributing to emission line shapes which are not present in absorption. This will be the subject of a future communication.

Finally, one must mention the anomalously large widths (10^3 times theoretical) observed by several workers (Tomiser, 1953, 1954; Moser & Schultz, 1959; Ya'akobi, 1966) in the broadening of alkali metal lines. There exists no theoretical explanation at the present time for these results, and they appear to be contradicted also by other experiments (Lauriston & Welsh, 1951; Chen, 1940; Watanabe, 1941; Gregory, 1942). It may be, therefore, that these results are in error, but it seems clear that more experimental work needs to be done.

10. *Discussion*

The theory developed here has the advantage of embracing all the commonly used approximations as special cases, and permitting a systematic study of validity criteria and corrections to them. The comparison with experiment is facilitated by obtaining closed form solutions for the limiting cases, and is, on the whole, satisfactory. Since the properties of the resolvent operator are important in many problems other than line shapes, it is hoped that some of the techniques developed here may have a wider applicability. A worthwhile direction for further work is the more quantitative study of the corrections to the approximations, particularly in the intermediate region between the impact and static limits.

It is worth pointing out that the differential equation and expansion used for the resolvent in this article is closely related to the similar treatment of the statistical operator $\exp(-\mathscr{H}/kT)$, which is standard in quantum statistical mechanics (Landau & Lifshitz, 1958). This is clear because the statistical operator is related to the resolvent by a Laplace transform. The relation of the resolvent to this and other operators encourages one to hope that some of the methods used here may be applicable to a wider class of problems.

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