of the atomic p-functions of Ga, As, and Ge; these can be estimated from atomic spectra to be 0.10, 0.30, and 0.20 ev for Ga, As, and Ge, respectively.[6] If we assume the same normalization factor for gallium arsenide, as seems appropriate for germanium in estimating the spin-orbit splitting in the solid from the free-atom value, we find that an electron at the top of the valence

band at $k=0$ spends more time on an arsenic atom than on a gallium atom.

Preliminary measurements of these bands as a function of temperature indicate the same qualitative temperature dependence observed in germanium.[1]

We wish to thank D. A. Kramer for his assistance in this work, E. O. Kane and F. Herman for valuable discussions, and D. A. Jenny and K. Weiser for several samples used in this investigation.

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[6] We wish to thank E. O. Kane for these estimates.

Simplified Quantum-Mechanical Theory of Pressure Broadening

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Quantum mechanics is used to treat the motion of the perturbers broadening a line. Several simplifying assumptions are made, such as the Born-Oppenheimer approximation, and the assumption of no degeneracy. These assumptions can be removed. Also made is the "impact approximation," which is essential for the validity of the results and cannot be removed. With it, the line has a Lorentz shape, and its width and shift are expressed in terms of the two scattering amplitudes of the perturbers by the atom in its upper and lower state. The case where the perturbers do not interact appreciably with the lower state is particularly simple. Then, the width and shift are proportional to the imaginary part and the real part of the forward scattering amplitude, respectively. A quantity called the "collision volume" is defined. It is shown that the impact approximation is valid only if the collision volume is much smaller than the volume per perturber. There is a second validity condition, which has no classical analog.

1. INTRODUCTION

PRESSURE broadening of spectral lines arises when an atom, molecule, or ion, which is emitting light in a gas, is disturbed by its interactions with the other constituents of the gas, such as other atoms, molecules, ions, or electrons. The study of this phenomenon is necessary for accurate spectroscopic observations, and it can in addition yield useful information about the conditions and concentrations in the gas. With the recent interest in high-temperature ionized gases, much thought has been given to using pressure broadening as a tool for measuring temperatures and ion or electron densities inside the gas. The theory of these effects has received a lot of attention in recent years.[1] Most theoretical work uses the "classical path approximation." It assumes that the "perturbers," i.e., the atoms, molecules, ions, or electrons that disturb the light-emitting object, move like classical particles, and, for simplicity, their trajectories are usually taken to be straight lines. Their effect on the line is then calculated using quantum mechanics. The classical path approximation is sometimes perfectly justified, particularly when the perturbers are heavy (i.e., not electrons).

By a "quantum-mechanical theory," we mean a theory where the motion of the perturbers is treated by quantum mechanics. The need for such a theory arises whenever the classical path approximation breaks down. This will happen, for instance, if the distance between the atom[2] and the nearest perturber is of the same order of magnitude as the wavelength of one or the other. Then, it is not a good approximation to replace the translational wave functions by wave-pockets moving according to the laws of classical mechanics. For light perturbers, like electrons, whose wavelength is therefore relatively large, this breakdown may occur for a sizable fraction of the total number of collisions. Thus, quantum-mechanical effects are important for a theory of electron broadening. Quantum mechanics must also be taken into account whenever the collision of a perturber with the atom is strongly inelastic, i.e., the energy transfer is not small compared to the kinetic energy. This will occur frequently in an ionized gas. Thus, it appears desirable to have a fully quantum-mechanical theory of pressure broadening, even if one is led to find afterwards that, in many cases, the classical path theory constitutes a good approximation to it.

The quantum-mechanical theory in this paper is "simplified" because several important approximations are made. These approximations are not really neces-

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[1] See the following reviews: A. Unsöld, *Physik der Sternatmosphären* (Springer-Verlag, Berlin, 1955), second edition, Chaps. 11 and 13; S. Ch'en and M. Takeo, Revs. Modern Phys. **29**, 20 (1957); R. G. Breene, Jr., Revs. Modern Phys. **29**, 94 (1957).

[2] We shall usually call the light-emitting object in the gas "the atom," even though it may be an ion or a molecule.

sary, and the author will publish at some later date a general theory from which they will have been removed. However, they are included here because they make the whole exposition very much simpler, and enable one to peer easily into the mechanism which generates the line shape. All the essential ingredients of the quantum-mechanical theory of pressure broadening are here. The assumptions in question consist in taking the states of the atom, between which the light is emitted, to be either nondegenerate, or such that all degenerate sub-states are affected by the perturbers in the same way. It is also assumed that the perturbers cannot make inelastic collisions with the atom, and that the elastic interaction potential between a perturber and the atom is a known function of the distance, which depends on the state of the atom. Those are the same assumptions that one usually makes in classical path calculations.[3] Admittedly, they are rather drastic, especially since we have mostly in mind electron perturbers. But consideration of this simple case first, makes it very much easier, later, to derive a theory that takes into account degeneracy, especially rotational degeneracy, inelastic collisions, and overlapping of lines.

There is one more approximation which is used in most of this paper (from Sec. 5 on), and which will not be removed in later work. It is the "impact approximation." It is a low-density or high-velocity approximation, consisting in saying that the average collision is weak.[4] Alternatively, one may say that the time interval between strong collisions is much longer than the duration of such collisions. It may also be characterized as the approximation under which an isolated line has a Lorentz shape. It is familiar in the classical path theory,[5] where it constitutes the opposite extreme to the "static approximation."[6] In the quantum-mechanical theory, on the other hand, there is no static approximation, and outside of the impact approximation very little can be said that is simple except for a few cases where the line turns out to have a Gaussian shape. The impact approximation constitutes an important limitation of our work, of course. We shall devote a large fraction of our time to investigating its *validity conditions*, a subject which has been very neglected.

It turns out to be very often valid when electron perturbers are involved.

The first use of quantum mechanics in pressure broadening theory was made by Weisskopf.[7] He wrote the wave function of the atom as the product of a translational wave function and an electronic wave function, and showed how the line shape resulted from application of the Franck-Condon principle. But he did not carry the quantum-mechanical theory any further. Instead, he derived the classical path theory from it, very elegantly, using a WKB approximation. The main difference between his work and our starting equations is that his translational wave function represents the motion of the atom only. Thus he considered a moving atom among fixed perturbers. Our translational wave function, on the other hand, will be a product of functions, one for each perturber. Our starting equations, and the ideas behind them, bear close similarity to the work of Jablónski.[8] But Jablónski, again, made no attempt to stay with quantum mechanics. Moreover, his work is marred by unnecessary, and sometimes inaccurate, approximations. The expressions giving the width and shift of the line in terms of quantum-mechanical phase shifts (Secs. 5 and 6) can be found in the work of Lindholm,[9] and have been quoted in the literature since. However, Lindholm's derivation is extremely sketchy. The present work is believed to be the first where the subject is treated completely, with particular emphasis put on the validity conditions. Finally, no review of quantum-mechanical theories of pressure broadening would be complete without mention of the work of Margenau and his collaborators.[10] Their work differs considerably from ours, in spirit as well as in some of the results. It is hoped that both approaches will prove useful in disentangling the complicated data on line shapes.

2. ASSUMPTIONS AND APPROXIMATIONS

We shall assume the atom fixed, with the perturbers moving around it. This is a good approximation for light perturbers, electrons for instance. The wave function for the whole system will be assumed to be the product of an internal wave function of the atom, and of a function of the center-of-mass coordinates of the perturbers. This type of wave function can be obtained by the Born-Oppenheimer approximation, which is the analog for this work of the adiabatic approximation in the classical path theory. It consists in solving the problem in two steps. First, we solve the Schrödinger equation for the atom, while holding the perturbers fixed at points x_1, x_2, $\cdots x_N$. Call $u(x_A,x_1,\cdots x_N)$ the atomic wave function, where x_A stands for all the in-

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[3] Exceptions are L. Spitzer, Phys. Rev. **55**, 699 (1939); **56**, 39 (1939); **58**, 348 (1940); P. W. Anderson, Phys. Rev. **76**, 647 (1949); A. C. Kolb, University of Michigan Engineering Research Institute, ASTIA Document No. AD 115 040 (unpublished).

[4] I.e., the change in the atomic wave function due to the collision is small.

[5] E. Lindholm, Arkiv Mat. Astron. Fysik **28B**, No. 3 (1941); **32A**, No. 17 (1945); H. M. Foley, Phys. Rev. **69**, 616 (1946); P. W. Anderson, reference 3; Phys. Rev. **86**, 809 (1952); T. Holstein, Phys. Rev. **79**, 744 (1950).

[6] By this we mean the approximation where one neglects the effect upon the line of the motion of the perturbers, as in the work of H. Holtsmark [Ann. Physik **58**, 577 (1919); Physik. Z. **20**, 162 (1919); **25**, 73 (1924)] and H. Margenau [Phys. Rev. **40**, 387 (1932); **48**, 755 (1935); **82**, 156 (1951)]. It is sometimes called the "statistical approximation," but this name does not seem appropriate, since statistics are just as important for the impact approximation as for this one.

[7] V. Weisskopf, Z. Physik **75**, 287 (1932).

[8] A. Jablónski, Phys. Rev. **68**, 78 (1945), and earlier papers quoted there.

[9] E. Lindholm, Arkiv Mat. Astron. Fysik **28B**, No. 3 (1941).

[10] Kivel, Bloom, and Margenau, Phys. Rev. **98**, 495 (1955); B. Kivel, Phys. Rev. **98**, 1055 (1955); R. E. Meyerott and H. Margenau, Phys. Rev. **99**, 1851 (1955).

ternal coordinates of the atom. Call $E + V_T(x_1, x_2, \cdots x_N)$ the energy, where E is the unperturbed energy. Both the wave function and the energy depend on $x_1, x^2, \cdots x_N$ as parameters. In the second step, we solve the Schrödinger equation for the motion of the perturbers in the potential $V_T(x_1, x_2, \cdots x_N)$. Call $\psi(x_1, x_2, \cdots x_N)$ the wave function, and ϵ_T the energy for this problem. Then the wave function for the total problem is taken to be $u(x_A, x_1, \cdots x_N)\psi(x_1, \cdots x_N)$, and the total energy $E + \epsilon_T$. Furthermore, we shall assume that the modifications induced in the atomic wave function u by the perturbers are small, and we shall neglect them. Thus, our wave function becomes

$$u(x_A)\psi(x_1, \cdots x_N), \tag{1}$$

where the first factor is the unperturbed atomic function.

It is customary to say that the Born-Oppenheimer approximation is not valid unless the particles whose coordinates are $x_1, \cdots x_N$ are much heavier than the internal constituents of the atom. This is not true if the perturbers are electrons. In that case, we must say that the wave function (1) agrees with the correct wave function only when the electrons are sufficiently distant from the atom. The near parts of the two functions may differ considerably. But our theory will still be valid if the line shape happens to be sensitive mostly to the distant parts of the wave function. In any event, this trouble will not arise in the complete theory which will follow this one, since the Born-Oppenheimer approximation will not be made there.

With respect to the potential $V_T(x_1, \cdots x_N)$, which determines the motion of the perturbers, we shall make two assumptions. The first is that the perturbers do not interact with each other. Each perturber interacts only with the atom, and is otherwise uncorrelated with the motion of the other perturbers. If we are talking about charged perturbers, this is true only of those that are inside the Debye radius, and we may have to introduce later a correction to take into account the mutual screening of the perturbers. The second assumption is to write the total interaction V_T as a sum of potentials, each of which involves only one perturber,

$$V_T(x_1, x_2, \cdots x_N) = V(x_1) + \cdots + V(x_N). \tag{2}$$

This "scalar additivity" assumption is known to be correct for certain types of interactions, such as van der Waals forces, but not so correct for some others, such as Stark interactions. In the latter case, it is the vector electric field which is a sum of contributions from each perturber. We have two reasons for assuming scalar additivity. The first is that it is the only simple assumption that can be made. This is true also of the classical path theories, where scalar additivity has usually been taken for granted, except in the static limit. The second reason is that we are interested mostly in the impact limit of the theory, and the complete discussion, to be published later, makes it

clear that the results of the impact approximation do not depend at all on the type of additivity that is assumed.

The determination of the potential $V(x)$ between a single perturber and the atom is a standard quantum-mechanical problem, whose solution, for every case, can be found in the literature. For instance, if the perturber is an electron, its exact interaction with the atom is the sum of Coulomb interactions with the various atomic constituents. If the distance between the atom and the perturber is fairly large, this can be replaced by the interaction of the atom with the electric field of the perturber, this field being assumed constant over the volume of the atom. The interaction energy is calculated using ordinary quadratic Stark-effect theory. There results the potential

$$V(r) = -ke^2/r^4, \tag{3}$$

k being the Stark constant, which depends on the state of the atom and increases rapidly as one goes to higher excited states. A more accurate potential can be derived, if necessary, by treating the interaction more accurately. Potential (3) is certainly incorrect for small r, and should be cut off appropriately near the atom.

3. THE LINE SHAPE

We shall compute the shape of the spontaneous emission line. The line shapes for induced emission and absorption can be deduced from it by the usual argument of Einstein[11] involving detailed balancing. It is known[12] that the lines resulting from the classical path theory do not always satisfy the principle of detailed balancing. But it can be shown[13] that the present work is in agreement with that principle.

The total power emitted in a dipole transition from initial state i to final state f is given by the well-known expression[14]

$$(4\omega^4/3c^3)|\langle f|d|i\rangle|^2, \tag{4}$$

where d is the dipole moment, c the speed of light, and ω the Bohr frequency,[15] $\omega = E_i - E_f$. Starting from (4), one should be able, by considering all possible initial and final states, to derive an expression for the power radiated per unit frequency interval, $P(\omega)$. As often happens in line-shape problems, it is actually easier to compute the Fourier transform of the line shape than the line shape itself. We shall compute the Fourier transform of $(3c^3/4\omega^4)P(\omega)$, which we call $\Phi(s)$,

$$\Phi(s) = \int_{-\infty}^{+\infty} (3c^3/4\omega^4)P(\omega)e^{-i\omega s}d\omega. \tag{5}$$

[11] A. Einstein, Physik. Z. 18, 121 (1917).

[12] S. Bloom and H. Margenau, Phys. Rev. 90, 791 (1953).

[13] M. Baranger, Rand Corporation Report No. RM-2118-AEC, Sec. (III, 13) (unpublished).

[14] L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1955), second edition, p. 261.

[15] We shall use a system of units such that $\hbar = 1$. Thus, we shall make no distinction between an energy and an angular frequency, or between a momentum and a wave vector.

$P(\omega)$ may be obtained by the inverse formula

$$(3c^3/4\omega^4)P(\omega)=F(\omega)=(2\pi)^{-1}\int_{-\infty}^{+\infty}\Phi(s)e^{i\omega s}ds. \quad (6)$$

What we shall call the line shape is $F(\omega)$, rather than $P(\omega)$ itself. Since $F(\omega)$ must be real, $\Phi(s)$ obeys the equation

$$\Phi(-s)=\Phi^*(s). \quad (7)$$

We shall always compute $\Phi(s)$ for positive s only, and use this condition to determine it for negative values of s.

Our initial and final wave functions have the form (1). With our assumption of scalar additivity, the perturbers' wave function $\psi(x_1,\cdots x_N)$ is a product,

$$\psi(x_1,\cdots x_N)=\psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N). \quad (8)$$

Each factor is a solution of a Schrödinger equation in potential V. There are two potentials, V_i and V_f, one for each state of the atom. The corresponding Schrödinger equations are

$$(K_1+V_i)\psi_{i1}(x_1)=\epsilon_1\psi_{i1}(x_1), \quad (9a)$$

$$(K_1+V_f)\psi_{f1}(x_1)=\epsilon_1'\psi_{f1}(x_1), \quad (9b)$$

where K_1 is the kinetic energy of perturber 1, and ϵ_1 and ϵ_1' its total energy in each case. Thus, the initial wave function for the whole system is

$$u_i(x_A)\psi_{ik_1}^+(x_1)\psi_{ik_2}^+(x_2)\cdots\psi_{ik_N}^+(x_N), \quad (10a)$$

with energy

$$E_i+\epsilon_1+\epsilon_2+\cdots+\epsilon_N, \quad (11a)$$

while the final wave function is

$$u_f(x_A)\psi_{fk_1'}^+(x_1)\psi_{fk_2'}^+(x_2)\cdots\psi_{fk_N'}^+(x_N), \quad (10b)$$

with energy

$$E_f+\epsilon_1'+\epsilon_2'+\cdots\epsilon_N'. \quad (11b)$$

In the above, the subscripts k_1, k_1', $\cdots$ stand for the wave vectors of the plane wave parts of each function. We have $\epsilon_1=k_1^2/2m$, etc.$\cdots$, m being the mass of a perturber. The superscript $+$ indicates that we chose outgoing scattered waves. This choice is completely arbitrary and does not affect the results. With these wave functions, expression (4) becomes[15a]

$$(4\omega^4/3c^3)|\langle u_f|d|u_i\rangle|^2|\langle\psi_{fk_1'}^+|\psi_{ik_1}^+\rangle|^2\cdots$$

$$\times|\langle\psi_{fk_N'}^+|\psi_{ik_N}^+\rangle|^2, \quad (12)$$

and the frequency of the light emitted is

$$(E_i-E_f)+(\epsilon_1-\epsilon_1')+\cdots+(\epsilon_N-\epsilon_N'). \quad (13)$$

The factor $|\langle u_f|d|u_i\rangle|^2$ in (12) is a constant, about which we can forget if we confine our interest to the shape of the line, and not its total intensity. The

important part of (12) is the overlap of the perturbers' wave functions in the initial state with those in the final state. It is seen that the reason why the frequency of the light differs from its unperturbed value E_i-E_f, is that some of the energy may be used for increasing or decreasing the total kinetic energy of the perturbers. Even if k differs from k', ψ_{ik}^+ and $\psi_{fk'}^+$ are not orthogonal, and their overlap determines the line shape. If V_i were identical to V_f, the overlap would be 0 unless k were identical to k', and then the frequency radiated would always be E_i-E_f and the line would be sharp.

From now on, we shall take the unperturbed line as the origin of frequencies, i.e., we shall forget about (E_i-E_f) in (13). In order to compute $\Phi(s)$, we do not need to know $P(\omega)$ explicitly. We may make a change of variables of integration in (5), and, instead of summing over ω, we sum over all final states and average over initial states.[16] ω is replaced by $(\epsilon_1-\epsilon_1')+\cdots+(\epsilon_N-\epsilon_N')$, and the power radiated is given by (12). The probability of occurrence of a certain initial state (i.e., the density matrix) is a product $\rho_{k1}\rho_{k2}\cdots\rho_{kN}$, where each ρ_k is equal to a constant times the Boltzmann factor $e^{-\epsilon/kT}$. Thus, except for a factor, $\Phi(s)$ is given by

$$\Phi(s)=\sum_{k_1\cdots k_N}\sum_{k_1'\cdots k_N'}\rho_{k1}\cdots\rho_{kN}|\langle\psi_{fk_1'}^+|\psi_{ik_1}^+\rangle|^2\cdots$$

$$\times|\langle\psi_{fk_N'}^+|\psi_{ik_N}^+\rangle|^2\exp[-i(\epsilon_1-\epsilon_1'+\cdots+\epsilon_N-\epsilon_N')s].$$

$\Phi(s)$ turns out to be the Nth power of another function, $\varphi(s)$, which refers to a single perturber,

$$\Phi(s)=[\varphi(s)]^N, \quad (14)$$

$$\varphi(s)=\sum_{kk'}\rho_k|\langle\psi_{fk'}^+|\psi_{ik}^+\rangle|^2e^{-i(\epsilon-\epsilon')s}. \quad (15)$$

This situation could have been anticipated, since, with our assumption of scalar additivity, the perturbers affect the atom independently, and the total frequency shift is the sum of individual shifts due to each perturber. Each of these individual shifts has a probability distribution, whose Fourier transform is given by (15). To obtain the probability distribution of the total shift, we can use the well-known theorem[17] which states that, if N independent random variables have the same distribution, the Fourier transform of the distribution of their sum is obtained by raising to the Nth power the Fourier transform of an individual distribution.

Our aim must be, therefore, to compute $\varphi(s)$, the Fourier transform of the line shape due to a single perturber. Since, most of the time, this perturber is very far away from the atom and does not influence it, this line shape must consist mainly of a δ function at the origin. But there is a small correction, of order $\mathcal{U}^{-1}$, $\mathcal{U}$ being the volume of the container, assumed to be very large. This correction arises in those rare times

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[15a] Expressions related to (12) appear in the work of M. Rudkjobing [Ann. astrophys. 12, 229 (1949)] and Kivel, Bloom, and Margenau (reference 10, p. 498).

[16] All states are normalized to unity.
[17] H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, New Jersey, 1946), p. 188.

when the perturber happens to be close to the atom. Thus, $\varphi(s)$ must have the form

$$\varphi(s) = 1 - \mathcal{U}^{-1}g(s). \qquad (16)$$

To get $\Phi(s)$, we raise $\varphi(s)$ to the Nth power. If we call n the number of perturbers per unit volume ($n = N\mathcal{U}^{-1}$), we obtain

$$\Phi(s) = \exp[-ng(s)]. \qquad (17)$$

We must therefore put $\varphi(s)$ in the form (16). $F(\omega)$ will follow from (17) by a Fourier transformation. This very simple way of going from a one-perturber line shape to a many-perturber shape is also applicable to the classical path theory.

Let us introduce the notations,

$$H_i = K + V_i, \qquad (18a)$$

$$H_f = K + V_f. \qquad (18b)$$

H_i and H_f are the Hamiltonian of the perturber, when the atom is in its initial and final state, respectively. Using them, we can eliminate the final states explicitly from (15), in the following way:

$$\begin{aligned}\varphi(s) &= \sum_{kk'} \rho_k \langle \psi_{ik}^+ | \psi_{fk'}^+ \rangle e^{i\epsilon's} \langle \psi_{fk'}^+ | \psi_{ik}^+ \rangle e^{-i\epsilon s} \\ &= \sum_k \rho_k \langle \psi_{ik}^+ | e^{iH_f s} e^{-iH_i s} | \psi_{ik}^+ \rangle. \end{aligned} \qquad (19)$$

It is instructive to note the connection between (19) and the corresponding equation in the classical path theory, which is[18]

$$\varphi(s) = \left(\exp\left[-i \int_0^s \Delta V(t) dt \right] \right)_{Av}, \qquad (20)$$

with

$$\Delta V = V_i - V_f = H_i - H_f. \qquad (21)$$

One can show the following relation

$$e^{iH_f s} e^{-iH_i s} = \mathfrak{T}_\rightarrow \exp\left[-i \int_0^s \Delta V_H(t) dt \right], \qquad (22)$$

where ΔV_H is the Heisenberg operator associated with ΔV,

$$\Delta V_H(t) = e^{iH_i t} \Delta V e^{-iH_i t},$$

and $\mathfrak{T}_\rightarrow$ is the "anti-time-ordering operator," which orders operators according to the time in their argument, with time increasing from left to right. With the transformation (22), (19) and (20) become very similar, and it is evident how (19) becomes (20) if the classical approximation is valid, and one can replace the wave function of the perturber by a small wave packet. Another way of deriving the classical result is through the WKB approximation, as Weisskopf[7] did.

In all the preceding, we have never mentioned the natural width of the lines, i.e., we have neglected the reaction of the radiation on the system. It actually turns out, in the overwhelming majority of experimental

cases, that the pressure-broadened width is much larger than the natural width. Hence, we shall neglect the latter in all this work. Moreover, one can give the following argument to show that, in all cases where we observe the absorption or emission of light by a system in thermal equilibrium, the pressure broadening must be much more important than the natural broadening. If we are actually able to observe something besides the blackbody spectrum, it must mean that radiation is not in thermal equilibrium with the system. If it is not radiation that keeps the system in thermal equilibrium, it must be something else, namely interactions through collisions. And these interactions have to be strong enough to keep the system in thermal equilibrium, in spite of the disruptive effect of the non-equilibrium radiation. Therefore, they broaden the line much more than the radiation does.

4. EXPRESSION OF $\varphi(s)$ IN TERMS OF AN INTEGRAL FREE FROM SINGULARITIES

In order to simplify the writing, we shall often omit from (19) the average over initial states, in the remainder of this paper. This does not mean that we think this average unnecessary or unimportant. Actually, one can dispense with it only for a rough estimate. But the average always comes at the very end of a calculation. Whenever a result depends on the energy of the incoming perturber, it should be averaged with the Boltzmann factor, $e^{-\epsilon/kT}$. We shall sometimes remind the reader of this by writing a subscript Av on the important expressions.

Our first task is to put $\varphi(s)$ in the form (16). In (19), the wave function is normalized to unity. But it is more usual, for scattering wave functions, to normalize them to the volume of the container, $\mathcal{U}$. We do this, and write

$$\varphi(s) = \mathcal{U}^{-1} \langle \psi_{ik}^+ | e^{iH_f s} e^{-iH_i s} | \psi_{ik}^+ \rangle. \qquad (23)$$

Then, we transform $\varphi(s)$ by using the integral equation[19]

$$e^{iH_f s} e^{-iH_i s} = 1 - i \int_0^s dt\, e^{iH_f t} \Delta V e^{-iH_i t}. \qquad (24)$$

To prove this equation, note that it is true for $s = 0$, and that the derivatives of both sides with respect to s are equal. After substituting in (23) and taking $e^{-iH_i t}$ out of the matrix element, we find

$$\varphi(s) = 1 - i\mathcal{U}^{-1} \int_0^s dt\, e^{-i\epsilon t} \langle \psi_{ik}^+ | e^{iH_f t} \Delta V | \psi_{ik}^+ \rangle. \qquad (25)$$

Hence we have, in the notation of the previous section,

$$g(s) = i \int_0^s dt\, e^{-i\epsilon t} \langle \psi_{ik}^+ | e^{iH_f t} \Delta V | \psi_{ik}^+ \rangle. \qquad (26)$$

[18] P. W. Anderson, Phys. Rev. 86, 809 (1952).

[19] R. P. Feynman, Phys. Rev. 76, 749 (1949).

In order to express $g(s)$ in terms of an integral free from singularities, we substitute for $\langle \psi_{ik}{}^+ |$ the expression[20]

$$\langle \psi_{ik}{}^+ | = \langle \psi_{fk}{}^+ | + \langle \psi_{ik}{}^+ | \Delta V (\epsilon - H_f - i\eta)^{-1}. \quad (27)$$

This can be proved by multiplying to the right by $(\epsilon - H_f)$. η is an infinitesimally small number, whose role is to insure that the right-hand side of (27) contains only outgoing scattered waves. With this transformation, $g(s)$ becomes

$$g(s) = i \int_0^s dt\, e^{-i\epsilon t} \langle \psi_{fk}{}^+ | e^{iH_f t} \Delta V | \psi_{ik}{}^+ \rangle$$

$$+ i \int_0^s dt\, e^{-i\epsilon t} \left\langle \psi_{ik}{}^+ \middle| \Delta V \frac{e^{iH_f t}}{\epsilon - H_f - i\eta} \Delta V \middle| \psi_{ik}{}^+ \right\rangle. \quad (28)$$

In the first term, $e^{iH_f t}$ may be taken out of the matrix element, and cancels $e^{-i\epsilon t}$. In the second term, we introduce a complete set of intermediate states $\psi_{fk'}$, eigenstates of H_f and normalized per unit volume (the boundary condition at infinity need not be specified), and we rewrite the matrix element in the following form:

$$\int \frac{d^3 \mathbf{k}'}{8\pi^3} \langle \psi_{ik}{}^+ | \Delta V | \psi_{fk'} \rangle \frac{e^{i\epsilon' t}}{\epsilon - \epsilon' - i\eta} \langle \psi_{fk'} | \Delta V | \psi_{ik}{}^+ \rangle.$$

We have assumed that the Hamiltonian H_f does not have any bound states. If there are some, they should be included in the summation. Finally, we perform the integration over t. The result is

$$g(s) = is \langle \psi_{fk}{}^+ | \Delta V | \psi_{ik}{}^+ \rangle$$

$$+ \int \frac{d^3 \mathbf{k}'}{8\pi^3} |\langle \psi_{fk'} | \Delta V | \psi_{ik}{}^+ \rangle|^2 \frac{1 - e^{-i(\epsilon - \epsilon')s}}{(\epsilon - \epsilon')(\epsilon - \epsilon' - i\eta)}. \quad (29)$$

For reasonably behaved potentials, the matrix elements occurring in this expression are free from singularities for all values of $\mathbf{k}$ and $\mathbf{k}'$. Hence, if we know the wave functions, we can in principle compute $g(s)$, and hence the line shape, without meeting any unforeseen difficulties. The computational difficulties, however, will in general be tremendous. Fortunately, in most cases involving electrons as perturbers, the impact approximation can be made. We shall study it in the next section. But we wanted to show how the general problem could be solved completely, in the quantum-mechanical formulation, if one had sufficient incentive to go through the calculations. It is possible to write (29) in the form of a sum over partial waves, which makes it slightly simpler and contains only one-dimensional integrals.

In the classical path theory, there exists a simple approximation to $\varphi(s)$ when s is small. One replaces $\int_0^s \Delta V(t) dt$ in the exponential in (20) by $s\Delta V$. This is

the static approximation. Nothing comparable seems to exist in the quantum-mechanical theory. There is no particularly simpler form of (29) valid for small s, except a Taylor expansion. For the static approximation to be valid, the classical approximation must first be possible. One can show readily, then, that an approximation to the second term of (29) by stationary phase integration yields the result of the classical static theory, while the first term of (29) is negligible.

5. THE IMPACT APPROXIMATION

In order to make easier a physical understanding of the impact approximation, we shall first restrict our considerations to the case where the potential V_f vanishes. This is very often true in practice. The atom is smaller, more tightly bound, and less polarizable in its lower state than in the upper one, and V_f often turns out to be much smaller than V_i. Since V_f vanishes, we shall drop the subscript i on V_i, H_i, and $|\psi_{ik}{}^+\rangle$, and we shall replace $\langle \psi_{fk}{}^+ |$ by $\langle \mathbf{k} |$, since it is a simple plane wave.

Let us start again from Eq. (26):

$$g(s) = i \int_0^s dt\, e^{-i\epsilon t} \langle \psi_k{}^+ | e^{iKt} V | \psi_k{}^+ \rangle. \quad (30)$$

Now, $\langle \psi_k{}^+ | e^{iKt}$ is the result of letting $\langle \psi_k{}^+ |$ propagate for time t with the free Hamiltonian K. During this propagation, the scattered wave will recede from the origin, and no new scattered wave will be formed, so that $\langle \psi_k{}^+ | e^{iKt}$ looks very much like $\langle \mathbf{k} | e^{i\epsilon t}$, at least near the origin. At large distances, the two functions do not look alike, because the scattered wave has not had time to disappear. But we really want $\langle \psi_k{}^+ | e^{iKt}$ multiplied by $V | \psi_k{}^+ \rangle$, and $V | \psi_k{}^+ \rangle$ is a function that vanishes except near the origin. Hence, for large enough t, $\langle \psi_k{}^+ | e^{iKt} V | \psi_k{}^+ \rangle$ will look just like $e^{i\epsilon t} \langle \mathbf{k} | V | \psi_k{}^+ \rangle$. It follows that, if s is large enough, $g(s)$ can be approximated by

$$g(s) \simeq is \langle \mathbf{k} | V | \psi_k{}^+ \rangle, \quad (31)$$

which is just the first term of (29). Exactly how large s has to be, is a question which we shall answer later. And if the values of s that are important for the calculation of $F(\omega)$ happen to be those for which (31) is true, $F(\omega)$ will have a Lorentz shape. We shall devote the later sections of this paper to a rigorous examination of the conditions under which this is a good approximation. In the meantime, we shall look into the significance of (31) with more detail.

According to (17), $\Phi(s)$, for positive s, is given by

$$\Phi(s) = \exp(-in\langle \mathbf{k} | V | \psi_k{}^+ \rangle s). \quad (32)$$

The corresponding line shape is

$$F(\omega) = (w/\pi)[(\omega - d)^2 + w^2]^{-1}, \quad (33)$$

with

$$d = n \mathfrak{R} \langle \mathbf{k} | V | \psi_k{}^+ \rangle, \quad (34a)$$

$$w = -n \mathfrak{I} \langle \mathbf{k} | V | \psi_k{}^+ \rangle. \quad (34b)$$

[20] B. A. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950); M. Gell-Mann and M. L. Goldberger, Phys. Rev. 91, 398 (1953).

The symbols $\mathfrak{R}$ and $\mathfrak{I}$ stand for "real part" and "imaginary part," respectively. The quantity $\langle \mathbf{k} | V | \psi_{\mathbf{k}}^{+} \rangle$ is, except for a factor, the forward scattering amplitude. The exact relation between the scattering amplitude $f(\theta, \varphi)$ and the matrix element $\langle \mathbf{k}' | V | \psi_{\mathbf{k}}^{+} \rangle$, where $\mathbf{k}'$ has the length of $\mathbf{k}$ and makes angles θ and φ with it, is[21]

$$f(\theta, \varphi) = -(m/2\pi)\langle \mathbf{k}' | V | \psi_{\mathbf{k}}^{+} \rangle. \quad (35)$$

Hence, the shift d is proportional to the real part of the forward scattering amplitude, and the width w to its imaginary part,

$$d = -(2\pi n/m)\mathfrak{R}[f(0)]_{\text{Av}}, \quad (36a)$$

$$w = (2\pi n/m)\mathfrak{I}[f(0)]_{\text{Av}}. \quad (36b)$$

The Boltzmann average must be taken.

It should not be surprising that our result is expressed in terms of the forward scattering amplitude. If we look at the original expression (23) for $\varphi(s)$, which becomes here

$$\mathcal{V}\varphi(s) = \langle \psi_{\mathbf{k}}^{+} | e^{iKs}e^{-iHs} | \psi_{\mathbf{k}}^{+} \rangle, \quad (37)$$

and if we imagine that, instead of taking a stationary state $|\psi_{\mathbf{k}}^{+}\rangle$, we take a wave packet, then $e^{-iHs}|\psi_{\mathbf{k}}^{+}\rangle$ represents the wave packet propagated in potential V for time s, while $\langle \psi_{\mathbf{k}}^{+} | e^{iKs}$ is the wave packet propagated for the same time freely. When s is large, the inner product of the two should be very similar to the forward element of the scattering matrix. Indeed, the S matrix is [20]

$$\langle \mathbf{k}' | S | \mathbf{k} \rangle = \langle \mathbf{k}' | \mathbf{k} \rangle - 2i\pi\delta(\epsilon - \epsilon')\langle \mathbf{k}' | V | \psi_{\mathbf{k}}^{+} \rangle, \quad (38)$$

while our result for (37) is

$$\mathcal{V} - is\langle \mathbf{k} | V | \psi_{\mathbf{k}}^{+} \rangle. \quad (39)$$

The difference consists in replacing $\langle \mathbf{k} | \mathbf{k} \rangle$ by $\mathcal{V}$, and $2\pi\delta(\epsilon - \epsilon)$ by s, which is just what would happen if we were to restrict the integration in the calculation of the S-matrix to a finite volume $\mathcal{V}$ and a finite time s. Again, the question, how large must s be before this becomes a good approximation, will be answered later.

The width can also be expressed in terms of the total cross-section σ, by virtue of the optical theorem,[22] which can be written (Ω is the solid angle)

$$\mathfrak{I}f(0) = (k/4\pi)\int d\Omega |f(\Omega)|^2 = (k/4\pi)\sigma. \quad (40)$$

Thus,

$$w = (\tfrac{1}{2}nv\sigma)_{\text{Av}}, \quad (36c)$$

where v is the velocity of the perturbers, $v = k/m$.

This result for the width must be compared with that of the old Lorentz theory,[23] which says that the width is equal to the average collision frequency, i.e.,

[21] D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., New York, 1951), p. 545.
[22] L. I. Schiff, reference 14, p. 105.
[23] H. A. Lorentz, Proc. Roy. Acad. Sci. (Amsterdam) **8**, 591 (1906).

$w = (nv\sigma)_{\text{Av}}$. In spite of appearances, the two results do not contradict each other. The Lorentz theory is valid when the atom has a sharp boundary. If a perturber goes inside the boundary, it interacts very strongly and interrupts the radiation completely. If it stays outside, it does not disturb anything. Under these conditions, it is well known that, in the classical limit, the quantum-mechanical cross section equals twice the classical cross section, because it contains in addition the diffraction cross section. Hence, the two results are really identical.

The fact that, when the impact approximation is valid, the width and shift of the line can be expressed in terms of the forward scattering amplitude and the cross section, means that, if it should become possible, some day, to measure the scattering of electrons by excited atoms, one could predict the width and shift in terms of experimental data very easily. In the meantime, we may take the observed values of electron-induced widths and shifts as indirect measurements of the total and the forward differential cross sections. We shall show, in a later publication, that relations (36a, b) between the shift and width and the elastic forward scattering amplitude remain true when inelastic collisions can take place. Equation (36c) is also true, with σ the total cross section.

If V is spherically symmetrical, the scattering amplitude can be written, in a well-known fashion,[22] in terms of the scattering phase shifts, δ_l, for the individual angular momenta,

$$f(\theta) = (2ik)^{-1}\sum_l(2l+1)(e^{2i\delta_l}-1)P_l(\cos\theta). \quad (41)$$

For the forward scattering amplitude, we replace every Legendre polynomial by unity. Written in terms of the phase shifts, the shift and width become

$$d = -[(\pi n/mk)\sum_l(2l+1)\sin2\delta_l]_{\text{Av}}, \quad (42a)$$

$$w = [(\pi n/mk)\sum_l(2l+1)(1-\cos2\delta_l)]_{\text{Av}}. \quad (42b)$$

These are the equations that were given by Lindholm.[9] They bear a striking resemblance to the result of the classical impact theory, which is[9]

$$d = \int \sin\varphi \, d\nu, \quad (43a)$$

$$w = \int (1 - \cos\varphi) \, d\nu. \quad (43b)$$

In the above, the integral is taken over all possible kinds of collisions, i.e., every possible impact parameter, energy, etc. The differential $d\nu$ is the frequency with which a particular kind of collision occurs. The angle φ is given by the following integral, taken along the classical trajectory,

$$\varphi = \int_{-\infty}^{+\infty} V(t) \, dt. \quad (44)$$

A calculation of δ_l by the WKB approximation yields just $-\varphi/2$. To bring out the resemblance between (42) and (43), we may write (42) in the form

$$d=[\sum_l nv2\pi(l+\tfrac{1}{2})k^{-2}\sin(-2\delta_l)]_{\text{Av}}. \qquad (45)$$

In this equation, $nv2\pi(l+\tfrac{1}{2})k^{-2}$ represents the frequency of arrival of perturbers with angular momentum l, since $2\pi(l+\tfrac{1}{2})k^{-2}$ is approximately equal to the area between two circles of radii l/k and $(l+1)/k$, respectively. Thus (45) constitutes the natural extension of (43a), when one wishes to take into account the fact that, in quantum mechanics, angular momentum is quantized.

6. IMPACT APPROXIMATION WHEN BOTH ATOMIC STATES INTERACT WITH THE PERTURBERS

Now, we return to the general case where both V_i and V_f are important, and derive the impact result for it. We start again from (26). $\langle\psi_{ik}{}^+|e^{iH_f t}$ is the result of propagating the wave $\langle\psi_{ik}{}^+|$ for time t with the Hamiltonian H_f. During this propagation, the scattered part of the wave function gradually changes, and starts to look more and more like the scattered part of $\langle\psi_{fk}{}^+|$, at least near the origin. At large distances, the scattered wave is still that of $\langle\psi_{ik}{}^+|$, as long as t is finite. But since this has to be multiplied by $\Delta V|\psi_{ik}{}^+\rangle$, which vanishes at large distances, the matrix element $\langle\psi_{ik}{}^+|e^{iH_f t}\Delta V|\psi_{ik}{}^+\rangle$ becomes practically equal to $\langle\psi_{fk}{}^+|e^{i\epsilon t}\Delta V|\psi_{ik}{}^+\rangle$ for large enough t. When it is so, $g(s)$ takes the form

$$g(s)\simeq is\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle, \qquad (46)$$

and the line has a Lorentz shape, with the following shift and width:

$$d=n\mathfrak{R}\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle_{\text{Av}}, \qquad (47a)$$

$$w=-n\mathfrak{I}\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle_{\text{Av}}. \qquad (47b)$$

We shall see later how large s has to be before (46) becomes true.

These results can be expressed in terms of the scattering amplitudes f_i and f_f for the potentials V_i and V_f, respectively. To show this, we need the following equations,[20] valid for any potential V (p.v. denotes the principal value)

$$|\psi_k{}^+\rangle=|\mathbf{k}\rangle+(\epsilon-K+i\eta)^{-1}V|\psi_k{}^+\rangle, \qquad (48a)$$

$$\langle\psi_k{}^+|=\langle\mathbf{k}|+\langle\psi_k{}^+|V(\epsilon-K-i\eta)^{-1}, \qquad (48b)$$

$$(\epsilon-K+i\eta)^{-1}=\text{p.v.}(\epsilon-K)^{-1}-i\pi\delta(\epsilon-K), \qquad (49a)$$

$$(\epsilon-K-i\eta)^{-1}=\text{p.v.}(\epsilon-K)^{-1}+i\pi\delta(\epsilon-K). \qquad (49b)$$

We write our matrix element as the difference of two terms,

$$\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle=\langle\psi_{fk}{}^+|V_i|\psi_{ik}{}^+\rangle-\langle\psi_{fk}{}^+|V_f|\psi_{ik}{}^+\rangle.$$

In the first term, we use (48b), applied to $\psi_{fk}{}^+$. In the second term, we use (48a), applied to $\psi_{ik}{}^+$. Then we use (49). The result is

$$\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle=\langle\mathbf{k}|V_i|\psi_{ik}{}^+\rangle-\langle\psi_{fk}{}^+|V_f|\mathbf{k}\rangle$$
$$+2\pi i\langle\psi_{fk}{}^+|V_f\delta(\epsilon-K)V_i|\psi_{ik}{}^+\rangle. \qquad (50)$$

The last matrix element may be written

$$(2\pi)^{-3}\int d^3k'\langle\psi_{fk}{}^+|V_f|\mathbf{k}'\rangle\delta(\epsilon-\epsilon')\langle\mathbf{k}'|V_i|\psi_{ik}{}^+\rangle,$$

and we can perform the integration over the length of $\mathbf{k}'$, by writing

$$d^3k'=mk'd\epsilon'd\Omega, \qquad (51)$$

thus leaving only an integral over solid angle Ω. Then, we use (35) and obtain (the star means complex conjugate):

$$\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle=-(2\pi/m)[f_i(0)-f_f{}^*(0)]$$
$$+iv\int d\Omega f_f{}^*(\theta,\varphi)f_i(\theta,\varphi). \qquad (52)$$

The shift is gotten from the real part of this expression:

$$d=\Big\{-(2\pi n/m)\mathfrak{R}[f_i(0)-f_f(0)]$$
$$+\tfrac{1}{2}inv\int d\Omega[f_f{}^*(\Omega)f_i(\Omega)-f_f(\Omega)f_i{}^*(\Omega)]\Big\}_{\text{Av}}. \qquad (53a)$$

The width is gotten from the imaginary part, which is

$$\mathfrak{I}\langle\psi_{fk}{}^+|\Delta V|\psi_{ik}{}^+\rangle=-(2\pi/m)\mathfrak{I}[f_i(0)+f_f(0)]$$
$$+\tfrac{1}{2}v\int d\Omega[f_f{}^*(\Omega)f_i(\Omega)+f_f(\Omega)f_i{}^*(\Omega)],$$

but this can be transformed by use of the optical theorem (40), and one obtains

$$w=\Big\{\tfrac{1}{2}nv\int d\Omega|f_i(\Omega)-f_f(\Omega)|^2\Big\}_{\text{Av}}. \qquad (53b)$$

Equations (53) give the shift and width of the line in terms of the two scattering amplitudes. This time, it is necessary to know the scattering amplitudes at all angles, not only in the forward direction. The width is still of the form $nv\sigma/2$, but the effective cross section σ that enters is obtained by taking the *difference* of the two scattering amplitudes, then squaring and integrating over angles. If f_i and f_f are identical, both shift and width vanish. If f_f vanishes, the results of the previous section are obtained.

Again we must point out the similarity between our results and expressions involving scattering matrices. We are trying to evaluate (23). Imagine that we take for wave functions some sort of wave packet. Then, we are asking for the inner product of the wave propa-

gated for time s with the Hamiltonian H_i, and of the same wave propagated for time s with the Hamiltonian H_f. The answer, for large s, must be the overlap of the two S matrices. The S matrices are[20] (we are taking the Hermitian conjugate of one of them)

$$\langle \mathbf{k}' | S_i | \mathbf{k} \rangle = \langle \mathbf{k}' | \mathbf{k} \rangle - 2\pi i \delta(\epsilon - \epsilon') \langle \mathbf{k}' | V_i | \psi_{i\mathbf{k}}^+ \rangle, \quad (54a)$$

$$\langle \mathbf{k} | S_f^\dagger | \mathbf{k}' \rangle = \langle \mathbf{k} | \mathbf{k}' \rangle + 2\pi i \delta(\epsilon - \epsilon') \langle \psi_{f\mathbf{k}}^+ | V_f | \mathbf{k}' \rangle. \quad (54b)$$

Their product is

$$\int (d^3k'/8\pi^3) \langle \mathbf{k} | S_f^\dagger | \mathbf{k}' \rangle \langle \mathbf{k}' | S_i | \mathbf{k} \rangle$$

$$= \langle \mathbf{k} | \mathbf{k} \rangle - 2\pi i \delta(\epsilon - \epsilon) \left[\langle \mathbf{k} | V_i | \psi_{i\mathbf{k}}^+ \rangle - \langle \psi_{f\mathbf{k}}^+ | V_f | \mathbf{k} \rangle \right.$$

$$+ 2\pi i \int (d^3k'/8\pi^3) \langle \psi_{f\mathbf{k}}^+ | V_f | \mathbf{k}' \rangle$$

$$\left. \times \delta(\epsilon - \epsilon') \langle \mathbf{k}' | V_i | \psi_{i\mathbf{k}}^+ \rangle \right]. \quad (55)$$

But, from (46) and (50), one sees that our result for $\mathcal{U}\varphi(s)$ is precisely the same as the right-hand side of (55), except for the replacement of $\langle \mathbf{k} | \mathbf{k} \rangle$ by $\mathcal{U}$ and of $2\pi\delta(\epsilon - \epsilon)$ by s.

The shift and width given by (53) can be expressed in terms of the two sets of scattering phase shifts, δ_{il} and δ_{fl}, by means of Eq. (41). However, using the considerations of the last paragraph about S matrices, we can guess what the result is going to be. The S matrix for an individual partial wave is $e^{2i\delta_l}$, i.e., if we send in the same ingoing wave as in a plane wave, we get out $e^{2i\delta_l}$ times the outgoing wave in a plane wave. The product of S_i and $S_f^\dagger$ is just $e^{2i(\delta_{il} - \delta_{fl})}$, for a given partial wave. Hence, we guess that the results will be the same as in the one-potential case, Sec. 5, except that the phase shift that appears there should be replaced by the difference between the two phase shifts. This is indeed what turns out. We obtain Lindholm's equations[9]:

$$d = -\{ (\pi n/mk) \sum_l (2l+1) \sin 2(\delta_{il} - \delta_{fl}) \}_{Av}, \quad (56a)$$

$$w = \{ (\pi n/mk) \sum_l (2l+1) [1 - \cos 2(\delta_{il} - \delta_{fl})] \}_{Av}. \quad (56b)$$

Again, these results constitute the natural quantum-mechanical extension of the classical results, which are again given by (43), but with φ defined by

$$\varphi = \int_{\infty}^{+\infty} \Delta V(t) dt. \quad (57)$$

7. THE COLLISION VOLUME

We shall devote most of the remainder of this paper to an investigation of the validity conditions of the impact approximation. The question which we really wish to answer is "When does the line have a Lorentz shape?" Whenever the shape is almost Lorentzian, we shall consider the impact approximation valid. In other words, we want the neglected terms to be small compared to the *width* of the line, not to the shift. If the shift is of the same order of magnitude as the width, or larger than it, it will also be given correctly by the approximation. If the shift calculated by the impact approximation turns out to be much smaller than the width, then it is not reliable, since there could be corrections of the same order of magnitude. But, in such a case, the shift is not interesting anyway.

Most of our considerations will be given for the case where one of the two potentials vanishes, as in Sec. 5. The general case is just as simple analytically, but is harder to picture in physical terms.

The nature of the validity condition is very simple. In Sec. 5, we saw that (31) could be expected to be true if s was large enough. This restriction on s will be written in the form

$$s \gg \tau, \quad (58)$$

and we shall call τ the "collision time." If the values of s that are important in determining the line shape happen to be much larger than τ, then the impact approximation is valid. Now, according to the impact approximation, the real exponential factor in $\Phi(s)$ is $\exp(-nv\sigma s/2)$ [see Eq. (36c)]; hence the values of s that are important are of order $(2/nv\sigma)$. Therefore, we want

$$2/nv\sigma \gg \tau, \quad (59)$$

or

$$U \ll n^{-1}, \quad (60)$$

with

$$U = \tfrac{1}{2} v\sigma \tau. \quad (61)$$

We shall call U the "collision volume." The validity condition, (60), can be stated: the collision volume must be much smaller than n^{-1}, the volume per perturber. We shall derive an explicit expression for U in the next section. Another way of stating the condition, according to (59), is: the width of the line, computed in the impact approximation, $nv\sigma/2$, must turn out to be much smaller than the inverse of the collision time. In this form, the validity condition is the same as in the classical path theory. Indeed, the collision time τ, as we shall calculate it, corresponds well in most cases to one's intuitive idea of a collision time.[24]

There is an additional validity condition, this one without classical analog. To show qualitatively how it arises, we imagine that we try to build a wave packet and to define a collision time in the classical manner. The smallest wave packet that can be built, without mixing waves of radically different energies, has a radius of order λ, the wavelength divided by 2π. Thus, a lower limit to the collision time is $2\lambda/v$, and a lower

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[24] However, τ may become infinite, if the cross-section σ happens to go through 0, as in the Ramsauer-Townsend effect. U, on the other hand, is always finite. For a definition of τ independent of that of U, see reference 13, Sec. (III, 9).

limit to the collision volume is $\sigma\lambda$. Hence we have the validity condition

$$\sigma\lambda \ll n^{-1}, \tag{62}$$

which we shall derive more rigorously in the next section.

Before deriving explicitly the expression for U, we want to try to guess at it. U must be positive, and can vanish only for a plane wave. It must give an idea of the volume in which the collision takes place, i.e., of the volume inside which the wave function propagates differently from that of a free particle of energy ϵ. An expression that fulfills these conditions is

$$U = \int d^3x \, |\psi_k^+(\mathbf{x}) - \bar{\psi}_k^+(\mathbf{x})|^2, \tag{63}$$

where $\bar{\psi}_k^+(\mathbf{x})$ is the "asymptotic wave function." This has the dimensions of a volume, since the plane wave part of ψ is normalized per unit volume. But what should we take for the asymptotic function? It seems too crude to take $e^{i\mathbf{k}\cdot\mathbf{x}} + f(\theta,\varphi)e^{ikr}/r$. On the other hand, if we take $\bar{\psi}_k^+(\mathbf{x})$ to be a function satisfying the Schrödinger equation for a free particle with energy ϵ everywhere except the origin, and equal to $\psi_k^+(\mathbf{x})$ at very large distances, then the integral in (63) does not converge near the origin, except for s waves. We solve this dilemma by going to momentum space. Call $\psi_k^+(\mathbf{k}')$ and $\bar{\psi}_k^+(\mathbf{k}')$ the Fourier transforms of $\psi_k^+(\mathbf{x})$ and $\bar{\psi}_k^+(\mathbf{x})$, respectively. Then, we also have

$$U = \int (d^3k'/8\pi^3) \, |\psi_k^+(\mathbf{k}') - \bar{\psi}_k^+(\mathbf{k}')|^2. \tag{64}$$

$\psi_k^+(\mathbf{k}')$ has the following form[20]:

$$\psi_k^+(\mathbf{k}') = \langle \mathbf{k}'|\mathbf{k}\rangle + (\epsilon - \epsilon' + i\eta)^{-1}\langle \mathbf{k}'|V|\psi_k^+\rangle. \tag{65}$$

$\langle \mathbf{k}'|V|\psi_k^+\rangle$ is a smooth function of $\mathbf{k}'$, which vanishes for large $|\mathbf{k}'|$. The part of it that is "on the energy shell," i.e., for which $|\mathbf{k}'| = |\mathbf{k}|$, determines the form of $\psi_k^+(\mathbf{x})$ at large distances, i.e., the scattering amplitude. The off-shell part of $\langle \mathbf{k}'|V|\psi_k^+\rangle$ determines $\psi_k^+(\mathbf{x})$ at finite distances. We shall define $\bar{\psi}_k^+(\mathbf{k}')$ by

$$\bar{\psi}_k^+(\mathbf{k}') = \langle \mathbf{k}'|\mathbf{k}\rangle + (\epsilon - \epsilon' + i\eta)^{-1}\langle \mathbf{k}''|V|\psi_k^+\rangle, \tag{66}$$

where $\mathbf{k}''$ is a vector whose direction is that of $\mathbf{k}'$, but whose length is the same as that of $\mathbf{k}$. Thus, $\bar{\psi}_k^+$ is determined solely by the scattering amplitude, and can fairly be called the asymptotic wave function. We obtain $\bar{\psi}_k^+(\mathbf{x})$ from

$$\bar{\psi}_k^+(\mathbf{x}) = \int (d^3k'/8\pi^3)e^{i\mathbf{k}'\cdot\mathbf{x}}\bar{\psi}_k^+(\mathbf{k}'). \tag{67}$$

Near the origin, its singularity is only of order $1/r$, and hence the integral in (63) is convergent.

8. THE VALIDITY CONDITIONS

In this section, we shall verify that the collision volume given by (63), (64), (66), is indeed such that, when (60) is true, the impact approximation is valid. We shall start from the exact expression for $g(s)$ [see Eq. (29)],

$$g(s) = is\langle \mathbf{k}|V|\psi_k^+\rangle$$
$$+ \int \frac{d^3k'}{8\pi^3} |\langle \mathbf{k}'|V|\psi_k^+\rangle|^2 \frac{1 - e^{-i(\epsilon-\epsilon')s}}{(\epsilon-\epsilon')(\epsilon-\epsilon'-i\eta)}, \tag{68}$$

and we shall examine under what conditions it can be replaced by its first term, as in (31).

First, we shall compare the real parts of (68) and (31). According to the optical theorem, (40), the real part of (31) is

$$-s\,\mathcal{I}\langle \mathbf{k}|V|\psi_k^+\rangle = \tfrac{1}{2}v\sigma s$$
$$= \int (d^3k'/8\pi^3) \, |\langle \mathbf{k}'|V|\psi_k^+\rangle|^2 \pi s\delta(\epsilon-\epsilon'). \tag{69}$$

On the other hand, one sees easily, using (49b), that the real part of (68) is equal to

$$\int (d^3k'/8\pi^3) \, |\langle \mathbf{k}'|V|\psi_k^+\rangle|^2 2(\epsilon-\epsilon')^{-2} \sin^2(\epsilon-\epsilon')s/2. \tag{70}$$

Therefore, the question is: can we replace $2(\epsilon-\epsilon')^{-2} \times \sin^2(\epsilon-\epsilon')s/2$ by $\pi s\delta(\epsilon-\epsilon')$? The two functions are indeed very similar. The first one is strongly peaked near $\epsilon-\epsilon'=0$, and integrates to πs (s is positive). Its width is of order s^{-1}. The replacement is legitimate if $|\langle \mathbf{k}'|V|\psi_k^+\rangle|^2$ does not vary very much when ϵ' changes by amounts of order s^{-1}, near the energy shell. If we call $\delta\epsilon$ the amount by which ϵ' must differ from ϵ before $|\langle \mathbf{k}'|V|\psi_k^+\rangle|^2$ has changed by an appreciable fraction of itself, $\delta\epsilon^{-1}$ must therefore be our collision time.

But we wish to give a more precise argument. We shall take the difference between (69) and (70), and require that it be small compared to (69). With $\mathbf{k}''$ defined in the same way as in the last section, the right-hand member of (69) may be written

$$\int (d^3k'/8\pi^3) \, |\langle \mathbf{k}''|V|\psi_k^+\rangle|^2 2(\epsilon-\epsilon')^{-2} \sin^2[(\epsilon-\epsilon')s/2], \tag{71}$$

since the matrix element is not involved in the integral over ϵ'. This is true with one reservation, namely that ϵ be much larger than s^{-1}. This is because $2(\epsilon-\epsilon')^{-2} \times \sin^2[(\epsilon-\epsilon')s/2]$ integrates to πs only when ϵ' goes from $-\infty$ to $+\infty$. In (71), it goes only from 0 to ∞. In order to insure that most of the contribution to (71) comes from positive ϵ', we require

$$s \gg \epsilon^{-1}. \tag{72}$$

The difference between (70) and (71) can be written

$$\int (d^3k'/8\pi^3)[\,|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\,]$$

$$\times [\,|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| + |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\,]$$

$$\times 2(\epsilon - \epsilon')^{-2}\sin^2[(\epsilon - \epsilon')s/2].$$

According to Schwartz's inequality, this is smaller than

$$\left\{\int \frac{d^3k'}{8\pi^3}[\,|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\,]^2\right.$$

$$\times \frac{2\sin^2[(\epsilon - \epsilon')s/2]}{(\epsilon - \epsilon')^2}\Big\}^{\frac{1}{2}}\left\{\int \frac{d^3k'}{8\pi^3}[\,|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\right.$$

$$\left. + |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\,]^2\frac{2\sin^2[(\epsilon - \epsilon')s/2]}{(\epsilon - \epsilon')^2}\right\}^{\frac{1}{2}}.$$

For the integral in the first curly bracket, we may replace $2\sin^2[(\epsilon - \epsilon')s/2]$ by its average value, 1, since the rest of the integrand does not have any singularity for $\epsilon - \epsilon' = 0$. The integral in the second curly bracket is the sum of (70), (71), and a cross term. In it, we can replace $2(\epsilon - \epsilon')^{-2}\sin^2[(\epsilon - \epsilon')s/2]$ by $\pi s\delta(\epsilon - \epsilon')$ for an estimate of the error. It is then equal to four times (69). Thus, the difference between the exact expression, (70), and the approximate one, (69) or (71), is smaller than

$$2\left[\frac{v\sigma s}{2}\right]^{\frac{1}{2}}\left[\int \frac{d^3k'}{8\pi^3}\left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\right)^2\right]^{\frac{1}{2}}.$$

$$(73)$$

This must be much smaller than one of them, say (69). Hence we require

$$4\int \frac{d^3k'}{8\pi^3}\left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\right)^2 \ll \frac{v\sigma s}{2}. \quad (74)$$

Before discussing the significance of this, we shall compare the imaginary parts of (68) and (31). Their difference is the imaginary part of the second term in (68), which is

$$\int (d^3k'/8\pi^3)|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|^2$$

$$\times \mathrm{p.v.}(\epsilon - \epsilon')^{-2}\sin[(\epsilon - \epsilon')s]. \quad (75)$$

We require that this be much smaller than the real part of (31), i.e., (69), since we want the corrections to be small compared to the width of the line. The procedure will be very similar to the one followed in case of the real parts. We may write, if condition (72) is satisfied,

$$\int (d^3k'/8\pi^3)|\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|^2$$

$$\times \mathrm{p.v.}(\epsilon - \epsilon')^{-2}\sin[(\epsilon - \epsilon')s] = 0, \quad (76)$$

since the integrand is an odd function of $(\epsilon - \epsilon')$. Thus, (75) can be written

$$\int \frac{d^3k'}{8\pi^3}\left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\right)$$

$$\times \left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| + |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\sin[(\epsilon - \epsilon')s]\right).$$

According to Schwartz's inequality, this is smaller than

$$\left\{\int \frac{d^3k'}{8\pi^3}\left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\right)^2\right\}^{\frac{1}{2}}$$

$$\times \left\{\int \frac{d^3k'}{8\pi^3}[\,|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\right.$$

$$\left. + |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|\,]^2\frac{\sin^2[(\epsilon - \epsilon')s]}{(\epsilon - \epsilon')^2}\right\}^{\frac{1}{2}}.$$

In the second curly bracket, we shall approximate $(\epsilon - \epsilon')^{-2}\sin^2[(\epsilon - \epsilon')s]$ by $\pi s\delta(\epsilon - \epsilon')$, since both functions have the same integral. Then, our estimate for the difference between the imaginary parts becomes identical with (73), the estimate for the difference between the real parts.

Thus, the two conditions that make (31) a good approximation to (68) are (72) and (74). We saw in Sec. 7 that the values of s that are of importance are of order $2/nv\sigma$; hence we substitute this in our conditions. (72) becomes $v\sigma/2\epsilon \ll n^{-1}$, which is the same as (62), since $\epsilon = k^2/2m = v/2\lambda$. Condition (74) becomes

$$4\int \frac{d^3k'}{8\pi^3}\left(\frac{|\langle \mathbf{k}'|\,V\,|\psi_{\mathbf{k}}{}^+\rangle| - |\langle \mathbf{k}''|\,V\,|\psi_{\mathbf{k}}{}^+\rangle|}{\epsilon - \epsilon'}\right)^2 \ll n^{-1}; \quad (77)$$

therefore the left-hand side must be the collision volume. The use of Schwartz's inequality in deriving (77) implies that our collision volume is an overestimate. It can be shown that, in certain cases, the factor 4 on the left-hand side of (77) is not necessary. On the other hand, there are other cases where it must be kept. Since (77) must be understood as a strong inequality anyway, this slight arbitrariness is not of too great importance. In many of the qualitative discussions, later in this work, we shall omit the 4. But we should put it in if we want to be on the safe side. We shall modify the collision volume further, by replacing the difference of the absolute values by the absolute value of the difference. The result is always larger, but much

more tractable. Thus, U will be defined by

$$U = \int \frac{d^3k'}{8\pi^3} \left| \frac{\langle \mathbf{k}' | V | \psi_\mathbf{k}{}^+ \rangle - \langle \mathbf{k}'' | V | \psi_\mathbf{k}{}^+ \rangle}{\epsilon - \epsilon'} \right|^2, \quad (78)$$

which is the very definition we gave in Sec. 7. Then, the second validity condition is

$$4U \ll n^{-1}, \quad (79)$$

which is the same as (60), except for the factor 4.

9. ANALYSIS IN PARTIAL WAVES

When the potential V is spherically symmetric, the collision volume can be written as a sum of contributions from the various partial waves,

$$U = \sum_l U_l. \quad (80)$$

The transformations that lead from the plane wave representation to the partial wave representation are completely standard, and therefore we shall only give the result, which is

$$U_l = 4\pi \lambdabar^2 (2l+1) \int_0^\infty [F_l(r) - \bar{F}_l(r)]^2 dr. \quad (81)$$

In this, $F_l(r)$ is the radial wave function for the lth partial wave, according to the expansion

$$\psi_\mathbf{k}{}^+(\mathbf{x}) = \sum_l (2l+1) i^l e^{i\delta_l} P_l(\cos\theta)(kr)^{-1} F_l(r). \quad (82)$$

$F_l(r)$ vanishes at the origin, and outside of the region of interaction it is equal to

$$\cos\delta_l \, f_l(kr) - \sin\delta_l \, g_l(kr), \quad (83)$$

where f_l and g_l are defined in terms of spherical Bessel and Neumann functions,[25] j_l and n_l, by

$$f_l(x) = x j_l(x), \quad g_l(x) = x n_l(x). \quad (84)$$

On the other hand, $\bar{F}_l(r)$ is what we called the asymptotic wave function, and it is equal, for all radii, to

$$\cos\delta_l \, f_l(kr) - \sin\delta_l \, \bar{g}_l(kr), \quad (85)$$

where $\bar{g}_l$ is defined by

$$\bar{g}_l(x) = 2\pi^{-1} \, \mathrm{p.v.} \int_0^\infty (x^2 - y^2)^{-1} f_l(y) y \, dy. \quad (86)$$

$\bar{g}_l(x)$ is approximately equal to $g_l(x)$ for large x. But for small x, while g_l blows up like x^{-l}, $\bar{g}_l$ stays finite. For even l, the difference between $\bar{g}_l$ and g_l is a polynomial in x^{-2}, which just removes the singularity of g_l at the origin. For odd l, the relation between the two functions is more complicated.

We may define a "collision range," ρ_l, as the ratio of U_l to σ_l, the partial cross section, which is

[25] L. I. Schiff, reference 14, p. 77.

$4\pi \lambdabar^2 (2l+1) \sin^2 \delta_l$:

$$\rho_l = U_l / \sigma_l = (\sin\delta_l)^{-2} \int_0^\infty [F_l(r) - \bar{F}_l(r)]^2 dr. \quad (87)$$

This range bears some resemblance to the "effective range" of nuclear physicists.[26] However, it differs from it by the fact that we are using the square of the difference between the two functions, while they use the difference of the squares. Our range vanishes only when the potential vanishes, while the effective range may vanish in other cases.

In an actual problem, if the number of angular momenta that contribute to the scattering is small, or if there are some important resonances, one must estimate U by looking separately at every angular momentum. In going through a resonance, in particular, the amplitude of the wave function inside the potential increases sharply, and the collision volume is correspondingly increased. But if a large number of angular momenta are effective, it is often possible to make some simple, general statements.

Such is the case when there are many angular momenta for which the phase shift is very large. This may happen, for instance, with the potentials proportional to a negative power of r, that are often used in pressure broadening work. Let us say that the phase shift is large for all angular momenta smaller than $r_0/\lambdabar$. Then, one can show that these angular momenta contribute $4\pi r_0^3/3$ to the collision volume, which is just what one would expect. There is still a small contribution from larger angular momenta, but this is never very large with the type of potential that we mentioned. Hence we want $4\pi r_0^3/3$ to be much smaller than n^{-1}. In other words, the impact parameter for which the phase shift if unity must be much smaller than the radius of a sphere of volume n^{-1}. This is the same as the classical validity condition. Indeed, this is a classical problem. Condition (62) is redundant in that case, since σ is of order r_0^2, and $\lambdabar$ is certainly much smaller than r_0.

Another important case is that in which many angular momenta are effective but the phase shifts are all small. This might happen, for instance, if the potential is of the "finite range" variety, for instance exponential or square well, with a range much larger than the wavelength. Since all phase shifts are small, the Born approximation is valid, and we can replace the matrix element $\langle \mathbf{k}' | V | \psi_\mathbf{k}{}^+ \rangle$, in the definition of the collision volume, by $\langle \mathbf{k}' | V | \mathbf{k} \rangle$. It follows from the properties of Fourier transforms that this varies by an appreciable fraction of itself when k' varies by amounts of order a^{-1}, where a is the range of the potential. The corresponding variations in ϵ' are of order v/a. We saw at the beginning of Sec. 8 that this was the inverse of

[26] H. A. Bethe and P. Morrison, *Elementary Nuclear Theory* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 55.

the collision time. Hence, the collision volume is $U = v\sigma\tau/2 = \sigma a/2$, and validity condition (79) becomes

$$2\sigma a \ll n^{-1}. \tag{88}$$

Condition (62) is redundant again, since a must be much larger than λ.

10. VALIDITY OF THE IMPACT APPROXIMATION WHEN V_f DOES NOT VANISH

When V_f is not negligible, the analysis of the last three sections can still be followed, with only minor changes. The validity conditions are still (62) and (79), but σ and U must now be defined as follows:

$$\sigma = -2v^{-1}\mathcal{I}\langle\psi_{fk}^{+}|\Delta V|\psi_{ik}^{+}\rangle$$

$$= 2w/nv = \int d\Omega |f_i(\Omega) - f_f(\Omega)|^2$$

$$= 4\pi\lambda^2 \sum_l (2l+1) \sin^2(\delta_{il} - \delta_{fl}), \tag{89}$$

$$U = \int \frac{d^3k'}{8\pi^3} \left| \frac{\langle\psi_{fk'}|\Delta V|\psi_{ik}^{+}\rangle - \langle\psi_{fk''}|\Delta V|\psi_{ik}^{+}\rangle}{\epsilon - \epsilon'} \right|^2$$

$$= \tfrac{1}{2}v\sigma\tau. \tag{90}$$

The last line defines τ. We have assumed that V_f did not have any bound states. If it does, they should be included in the summation over $\mathbf{k'}$.

In order to understand these results, we must realize that it is only the difference between the two potentials, ΔV, that is effective in broadening or shifting the line. Hence, σ is the cross section that one would compute starting from the difference between the two scattering amplitudes, or the difference between the two phase shifts. We might call it the "effective collision cross section," or the "optical cross section." It may be much smaller than the individual cross sections σ_i and σ_f, for potentials V_i and V_f, respectively. Similarly, U may be much smaller than U_i or U_f, computed according to Sec. 8. This is because U is not the volume of space where ψ_{ik}^{+} differs appreciably from a free wave function, but only the volume where it differs appreciably from an eigenfunction of H_f. The situation with respect to the collision times is different. A little reflection will show that τ can be expected to be of the same order of magnitude as τ_i or τ_f, whichever is

larger. From this estimate of τ, one obtains a convenient estimate of U, through multiplication by $v\sigma/2$.

It may happen that τ_i, τ_f, U_i, U_f, σ_i, and σ_f cannot be defined, while τ, U, and σ exist. This is the case, for instance, if the line is emitted by an ion. Both V_i and V_f contain the long-range Coulomb interaction between the ion and the charged perturbers. But the expressions for σ and U still converge to finite results, although more care is needed in making simple estimates.

11. CONCLUSION

We hope to have shown by this work, that it is possible to make a quantum mechanical theory of pressure broadening, along the same lines as the classical path theory. Even if our initial approximations were not absolutely accurate, they were worth making in order to show the basic simplicity of the theory, and its similarity with well-known classical theories based on equivalent assumptions. They can be removed, and this will be done in another paper.

We also hope to have given the reader a feeling for the impact approximation and its region of validity. One last word is called for here. Conditions (60) or (79) state that the collision volume is much smaller than the volume per perturber. Hence, at any given time, the average number of perturbers inside the collision volume is much smaller than unity. This seems to imply that the collisions occur one at a time, and are separated by large time intervals. This is true, provided that, by the word "collisions," we mean "strong collisions." Otherwise, it is a very misleading statement, because weak collisions, i.e., those with small phase shifts, do not make a full contribution to the collision volume, and it is perfectly possible to have several weak collisions going on at the same time, without necessarily endangering the validity of the impact approximation. It remains true, however, that this approximation is a low-density limit, and if n is increased too much it will eventually stop being valid.