and Sah and Shockley[11] have indicated how τ_n and τ_p can be obtained when there is more than one trap level in the forbidden gap.

At surfaces where surface recombination is important, one may put, for the components of the carrier current densities perpendicular to that surface,

$$J_{e1}=-J_{h1}=ens_n=eps_p,$$

in analogy with (2); these boundary conditions define the surface recombination velocities s_n and s_p, which, of course, may or may not be equal.

As a final application of the theory, consider the case of the steady-state PEM current when the light is absorbed in the bulk within a distance which is at least comparable to carrier diffusion lengths but which is still small compared to the thickness of the sample. For this purpose, it is convenient to define what might be called the "effective ambipolar magnetic diffusion length,"

$$L_D^*=\left[\frac{D\tau_{\mathrm{PEM}}(1+c)}{1+\mu^2B^2+bc(1+\mu^2B^2/b^2)}\right]^{\frac{1}{2}}. \tag{8}$$

With no magnetic field, L_D^* reduces to the diffusion length of the minority carrier in an extrinsic semiconductor. Also, for the case when light is strongly absorbed at the surface of the material, the PEM current, as given by Eq. (4), can be written as

$$i_{\mathrm{PEM}}=\left(1+\frac{1}{b}\right)eI\mu BL_D^*. \tag{9}$$

If light (assumed to be monochromatic, for simplicity) is absorbed in the bulk, however, the term

$$-eI\alpha\exp(-\alpha y)$$

must be added to each of the right-hand sides of the recombination relations (2), representing the volume generation of electron-hole pairs by the light. Here, α is the optical absorption coefficient and y is the coordinate in the direction perpendicular to the illuminated surface. The PEM current is then found to be given by

$$i_{\mathrm{PEM}}=\left(1+\frac{1}{b}\right)eI\mu BL_D^*\frac{\alpha L_D^*}{1+\alpha L_D^*}. \tag{10}$$

When $\alpha L_D^*\gg 1$, (10) reduces to the expression (9), as it should, since the physical meaning of $\alpha L_D^*\gg 1$ is that the absorption of light takes place within a distance much smaller than the effective diffusion length L_D^*, i.e., the light is absorbed "at the surface." In short, (9) and (4) are a special case of (10).

The purpose here in exhibiting (10) is to show more clearly how lifetimes enter in steady-state diffusion processes, namely, by way of the effective diffusion length L_D^*. It is L_D^* (evaluated at the appropriate magnetic field) which determines the steady-state behavior of the PEM effect, the p-n junction effect, and other diffusion phenomena.

[11] C. T. Sah and W. Shockley, Phys. Rev. **109**, 1103 (1958).

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General Impact Theory of Pressure Broadening*

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The work of two previous papers is extended and a theory of pressure broadening is developed which treats the perturbers quantum mechanically and allows for inelastic collisions, degeneracy, and overlapping lines. The impact approximation is used. It consists in assuming that it takes, on the average, many collisions to produce an appreciable disturbance in the wave function of the atom, and it results in an isolated line having a Lorentz shape. Validity criteria are given. When the approximation is valid, it is allowable to replace the exact, fluctuating interaction of the perturbers with the atom by a constant effective interaction. The effective interaction is expressed in terms of the one-perturber quantum mechanical transition amplitudes on and near the energy shell and its close relationship to the scattering matrix is stressed. The calculation of the line shape in terms of the effective interaction is the same as when the perturbers move on classical paths. Results are written explicitly for isolated lines. If the interaction of the perturbers with the final state can be neglected, the shift and width are proportional to the real and imaginary part of the forward elastic scattering amplitude, respectively. By the optical theorem, the width can also be written in terms of the total cross section. When the interaction in the final state cannot be neglected, the shift and width are still given in terms of the elastic scattering amplitudes, in a slightly more complicated fashion. Finally, rules are given for taking into account rotational degeneracy of the radiating states.

1. INTRODUCTION

IN two previous papers,[1] the theory of pressure broadening has been extended in two different directions. In I, it was shown how the motion of the perturbers can be treated quantum mechanically, and the width and shift of the line were expressed in terms of the quantum-mechanical scattering amplitudes. But

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[1] M. Baranger, Phys. Rev. **111**, 481 (1958), referred to as I.

M. Baranger, Phys. Rev. **111**, 494 (1958), referred to as II. Many of the results of II have also been obtained by A. C. Kolb and H. Griem, Phys. Rev. **111**, 514 (1958).

the treatment was restricted to elastic collisions and nondegenerate states of the atom. In II, on the other hand, the perturbers followed classical paths but we allowed inelastic collisions, degeneracy, and overlapping lines. For a consistent theory of electron broadening, it is necessary to consider together quantum-mechanical perturbers, inelastic collisions, and overlapping lines; hence a synthesis of the two papers is called for. This is the purpose of the present work. The two previous papers have used the impact approximation and the present one will too. This consists essentially in saying that, on the average, it takes many collisions to produce an appreciable change in the wave functions of the atom, and it results in an isolated line having a Lorentz shape. Without this approximation, a program as general as the one we are now undertaking would be next to impossible to achieve. We shall carefully examine its validity conditions. It usually turns out to be valid in problems of electron broadening.

The main result of II was that, when the impact approximation is valid, it is allowable to replace the exact, fluctuating interaction between the atom and the perturbers by a constant effective interaction $\mathcal{C}$, which is not Hermitian, however. The very same statement will be seen to be true here. In II, $\mathcal{C}$ was related to the collision matrix S for a collision between a classical perturber and a quantum-mechanical atom. Here, on the other hand, $\mathcal{C}$ will follow from a solution of the fully quantum-mechanical scattering problem. In particular, the diagonal elements of $\mathcal{C}$ will be expressed in terms of the scattering amplitudes, in a generalization of the expressions for the width and shift given in I. Once this new quantum-mechanical $\mathcal{C}$ has been found, the remainder of the line shape calculation is identical with that of II and we shall not need to repeat it here. In particular, the simplifications due to spherical symmetry and the treatment of overlapping lines have already been given there. However, since the results for isolated lines are especially simple and important, we shall write them down explicitly in the last section of this paper.

All the results of this paper are expressed in terms of the quantum-mechanical transition amplitudes, on or near the energy shell, for the scattering of one perturber by the atom. The problem of computing these amplitudes is completely outside the scope of pressure broadening and we shall make no attempt to solve it. The reader is referred to the abundant literature on the subject. Let us say only that the problem can be quite difficult, and that no general method of solution exists, but in each case one must find the most suitable approximation method. Specific examples of electron broadening problems will be considered in future publications.

2. THE ONE-STATE CASE

It was shown in Sec. 2 of II that the intensity spectrum of the light, $P(\omega)$, is given by[2]

$$P(\omega)=(4\omega^4 n_+/3c^3)F(\omega), \tag{1}$$

$$F(\omega)=\pi^{-1}\Re\int_0^{+\infty} e^{i\omega s}\Phi(s)ds, \tag{2}$$

$$\Phi(s)=\mathrm{Tr}[\mathbf{d}T^*(s)\mathbf{d}T(s)\rho], \tag{3}$$

where $T(s)$ is the Schrödinger evolution operator,[3]

$$T(s)=e^{-iHs}, \tag{4}$$

ρ is the Boltzmann-Gibbs density matrix (normalized to unit trace),

$$\rho=Z^{-1}e^{-\beta H}, \tag{5}$$

Z is the partition function, H is the Hamiltonian operator for the whole system, which is the sum of the atomic Hamiltonian H_A, the kinetic energies of the N perturbers $\sum_j K_j$, and the N interactions,

$$H=H_A+\sum_j K_j+\sum_j V_j, \tag{6}$$

and the other notations are as in II. We assume that the perturbers move completely independently, hence there is no term in the Hamiltonian to represent the interactions between the various perturbers. Equation (3) differs from (II, 10) in that it does not include the average over all possible types of motion of the perturbers, since this motion is already fully taken into account by the Hamiltonian (6). In view of the fact that the Hamiltonian is time-independent, it is possible to give a derivation of (3) simpler than that of II and based on the standard expression [for instance (I, 4)] for the power emitted by a stationary quantum state, but this is left to the reader.[4]

As before, we shall consider first the case where only the initial state of the atom is affected by its interaction with the perturbers, which we call the one-state case. Then, we replace $T^*(s)$ in (3) by $e^{iH_As}\exp(i\sum K_j s)$, but we can forget about the factor e^{iH_As} is we decide to take the energy of the final state of the atom as the origin of energies, which we shall do. Using definition (II, 12) of the operator D, and noting that $\exp(i\sum K_j s)$ commutes with $\mathbf{d}$, we can write

$$\Phi(s)=\mathrm{Tr}[D\exp(i\textstyle\sum K_j s)T(s)\rho]. \tag{7}$$

This is to be compared with Eq. (II, 13). The trace there involved only the atomic coordinates, while here it involves both the atom and the perturbers. On the other hand, we need no average sign in the present formula. Our aim will be to perform that part of the

[2] Throughout this paper, the asterisk means Hermitian conjugate. For an ordinary number, this is the same as the complex conjugate.

[3] We take $\hbar=1$.

[4] See, for instance, P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954), Appendix I.

trace which involves the perturber coordinates. Once this is done, it will be found that the remaining trace over the atomic coordinates is identical with the one occurring in II and can be treated by the same methods. We shall first focus our attention on the operator $\exp(i\sum K_j s)T(s)$. It is actually more convenient to consider the operator $\exp[i(H_A+\sum K_j)s]T(s)$ and to multiply it afterwards by $e^{-iH_A s}$. Later, we shall consider the problem of including the density matrix. Since D involves only the atomic coordinates, it never enters into our considerations. That part of the argument where D enters is the same as in II.

Consider the relation

$$\exp[i(H_A+\sum K_j)s]\exp[-i(H_A+\sum K_j+\sum V_j)s]$$
$$=\mathfrak{T}\exp\left[-i\int_0^s\sum V_j'(t)dt\right], \quad (8)$$

with the definition

$$V_j'(t)=e^{i(H_A+K_j)t}V_j e^{-i(H_A+K_j)t}. \quad (9)$$

This is the analog of (II, 16) and can be proved by taking the derivatives of both sides with respect to s. The operator $\mathfrak{T}$ is the time-ordering operator, as in II. The right-hand side of (8) can be rewritten in the form of a product of N factors, each of which refers to a particular perturber, as follows

$$\mathfrak{T}\exp\left[-i\int_0^s V_1'(t)dt\right]\cdots\exp\left[-i\int_0^s V_N'(t)dt\right]. \quad (10)$$

But this product is very hard to evaluate because each factor is an operator and the operation $\mathfrak{T}$ produces a very complicated entanglement[5] of these operators. However, the impact approximation is precisely the case in which they disentangle themselves naturally, just as in II. One can define a "collision time" τ, which corresponds roughly to the duration of an average collision, and the impact approximation is the case in which the time interval between strong collisions is much larger than τ. Hence the strong collisions are completely disentangled. As in II, entanglement does not arise for the weak collisions, because they can be treated by perturbation theory. The reader may be puzzled by the fact that we seem to have reverted to a classical language for describing the motion of the perturbers, while we should be talking about operators and wave functions. But the transition from the classical to the quantum-mechanical language may be effected by using Feynman's interpretation of quantum mechanics,[6] which says that the matrix element of an operator such as (8) may be looked upon as a sum of contributions from every classically describable path. If, for the great majority of paths that make an appreciable contribution to the matrix element, the collisions are disentangled, we may write the operator itself in disentangled form. We shall now proceed to translate these ideas into analytical language.

The exponential on the right-hand side of (8) may be expanded in a power series as follows

$$\sum_{m=0}^{\infty}\frac{(-i)^m}{m!}\mathfrak{T}\int_0^s dt_1\cdots\int_0^s dt_m\sum V_i'(t_1)\cdots\sum V_j'(t_m)$$
$$=\sum_{m=0}^{\infty}\sum_{i_1=1}^{N}\cdots\sum_{i_m=1}^{N}\frac{(-i)^m}{m!}\mathfrak{T}\int_0^s dt_1\cdots\int_0^s dt_m$$
$$\times V_{i_1}'(t_1)V_{i_2}'(t_2)\cdots V_{i_m}(t_m). \quad (11)$$

Each operator $V_i'(t)$ is also a function of the coordinates $\mathbf{x}_i$ of the perturber (as well as of the atomic coordinates), although they are not explicitly written. When a matrix element is taken, an integral over these coordinates is performed. Now, we can represent each term in the expansion (11) by a "Feynman diagram" in space-time. For each perturber i, we draw a trajectory obtained by joining those space-time points that enter as arguments of V_i in (11). We say that those are the points where the perturber interacts with the atom and that in between it propagates freely. A matrix element of (11) or (8) appears then as a sum of contributions from every possible Feynman diagram. It turns out that a diagram gives an appreciable contribution only if all interactions of a given perturber occur within a short enough time and we define the collision time as an order of magnitude for this time. Then it is clear that, if the perturber density is sufficiently low (the precise validity conditions will be given later), most of the important Feynman diagrams will have the collisions occurring one after another, in a completely disentangled manner.

Our next task must be, then, to estimate the collision time. For this, we consider a matrix element of an expression like (8), but for a single perturber. This is also a matrix element of one of the factors in (10). Consider first a diagonal matrix element (we omit the subscript j)

$$\langle a\mathbf{k}|e^{i(H_A+K)s}e^{-i(H_A+K+V)s}|a\mathbf{k}\rangle, \quad (12)$$

where $|a\rangle$ is an eigenstate of H_A and $|\mathbf{k}\rangle$ an eigenstate of K, namely a plane wave of momentum $\mathbf{k}$. We transform this using the integral equation

$$e^{-i(H_A+K+V)s}=e^{-i(H_A+K)s}$$
$$-i\int_0^s dt\, e^{-i(H_A+K)(s-t)}Ve^{-i(H_A+K+V)t}, \quad (13)$$

which can be proved by noting that it is true for $s=0$ and that the derivatives of both sides with respect to

[5] R. P. Feynman, Phys. Rev. **84**, 108 (1951).
[6] R. P. Feynman, Revs. Modern Phys. **20**, 367 (1948); Phys. Rev. **76**, 749 (1949).

s are equal. Then, (12) is equal to

$$\mathcal{V}-i\int_0^s dt\, e^{i(E_a+\epsilon)t}\langle a\mathbf{k}|\,Ve^{-i(H_A+K+V)t}|\,a\mathbf{k}\rangle, \quad (14)$$

where E_a is the energy of the atomic level, ϵ equals $k^2/2m$, the kinetic energy of the perturber, and $\mathcal{V}$ is the volume of the container. We normalize states of the perturber per unit volume. We can give an argument identical to that of Sec. 5 of I to approximate (14) for large s. We say that $e^{-i(H_A+K+V)t}|\,a\mathbf{k}\rangle$ is the result of propagating the eigenstate $|\,a\mathbf{k}\rangle$ of the unperturbed Hamiltonian H_A+K with the true Hamiltonian H_A+K+V for a time t. If t is large enough, $e^{-i(H_A+K+V)t}|\,a\mathbf{k}\rangle$ looks just like $e^{-i(E_a+\epsilon)t}|\psi_{a\mathbf{k}}{}^+\rangle$, at least for not too large distances. By $|\psi_{a\mathbf{k}}{}^+\rangle$, we mean an eigenstate of H_A+K+V, i.e., a scattering state, consisting of a plane wave $|\,\mathbf{k}\rangle$ ingoing upon the atom in state $|\,a\rangle$ and of various outgoing scattered waves, elastic and inelastic. Since the potential V occurs in the matrix element in (14), the behavior of $e^{-i(H_A+K+V)t}|\,a\mathbf{k}\rangle$ at large distances does not matter. Hence we can expect that, if s is large enough, (14) can be approximated by

$$\mathcal{V}-is\langle a\mathbf{k}|\,V|\psi_{a\mathbf{k}}{}^+\rangle, \quad (15)$$

which involves only the forward elastic scattering amplitude. Thus, if s is large enough, the matrix element (12) is simply related to the scattering matrix, and it is eminently reasonable to define the collision time,[7] as we did in I, as that value of s for which (15) begins to be a good approximation to (12). In order to estimate this time, we replace $|\,a\mathbf{k}\rangle$ in (14) by[8]

$$|\,a\mathbf{k}\rangle=|\psi_{a\mathbf{k}}{}^+\rangle-(E_a+\epsilon-H_A-K-V+i\eta)^{-1}V|\,a\mathbf{k}\rangle, \quad (16)$$

and (14) becomes equal to (15) plus the following correction

$$i\int_0^s dt\, e^{i(E_a+\epsilon)t}\langle a\mathbf{k}|\,Ve^{-i(H_A+K+V)t}\times(E_a+\epsilon-H_A-K-V+i\eta)^{-1}V|\,a\mathbf{k}\rangle. \quad (17)$$

After one introduces a set of intermediate states $\psi_{b\mathbf{k}'}$ eigenstates of H_A+K+V,[9] and one performs the integral over t, the correction becomes

$$\sum_b\int\frac{d^3k'}{8\pi^3}|\langle\psi_{b\mathbf{k}'}|\,V|\,a\mathbf{k}\rangle|^2\times\frac{e^{i(E_a+\epsilon-E_b-\epsilon')s}-1}{(E_a+\epsilon-E_b-\epsilon')(E_a+\epsilon-E_b-\epsilon'+i\eta)}. \quad (18)$$

[7] For another, equivalent definition of the collision time, directly in terms of the time intervals occurring in (11), see M. Baranger, The RAND Corporation Report No. RM-2118-AEC (unpublished), Sec. (V,3).

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

[9] The boundary condition at infinity need not be specified. Bound states should also be included in the summation if they exist.

As in I, we require that the correction be much smaller than the real part of $is\langle a\mathbf{k}|\,V|\psi_{a\mathbf{k}}{}^+\rangle$. The argument follows that of Sec. 8 of I with only minor modifications. We shall not reproduce it here since it is rather lengthy. The result is that the collision time τ is related to the "collision volume" U by

$$U=\tfrac{1}{2}v\sigma\tau. \quad (19)$$

U is given by

$$U=\sum_b\int\frac{d^3k'}{8\pi^3}\left|\frac{\langle\psi_{b\mathbf{k}'}|\,V|\,a\mathbf{k}\rangle-\langle\psi_{b\mathbf{k}''}|\,V|\,a\mathbf{k}\rangle}{E_a+\epsilon-E_b-\epsilon'}\right|^2, \quad (20)$$

where $\mathbf{k}''$ is a vector whose direction is that of $\mathbf{k}'$, but whose length is such that

$$E_a+\epsilon-E_b-\epsilon''=0. \quad (21)$$

σ is the total cross section

$$\sigma=(2\pi/v)\sum_b\int(d^3k'/8\pi^3)\times|\langle\psi_{b\mathbf{k}'}|\,V|\,a\mathbf{k}\rangle|^2\delta(E_a+\epsilon-E_b-\epsilon'). \quad (22)$$

In addition to this, however, the collision time can in no case be smaller than the reciprocal of the energy of the perturbers. This is condition (I, 72), but here we must include the energy of the inelastically scattered perturbers as well as the elastic ones. This condition is none else but the uncertainty principle.

It is not sufficient to consider a diagonal element of (8) as in (12). We are also going to need some off-diagonal elements. However, we must keep in mind that the interval between (strong) collisions is, on the average, much larger than the collision time, hence energy is almost conserved in the individual collisions and, according to the uncertainty principle, the only off-diagonal elements that we shall need are those for which the energy difference between the two states is much smaller than τ^{-1}. One can also see this in another way since, as in II, one of the validity conditions for the approximation is that the width of the lines be much smaller than τ^{-1}. It was shown in Sec. 5 of II that we need off-diagonal elements of the effective interaction $\mathfrak{IC}$ only when some lines overlap. For an isolated line, we may treat $\mathfrak{IC}$ by first-order perturbation theory and therefore require only the diagonal element. But overlap will not happen unless the two unperturbed energies differ by much less than τ^{-1}, hence those are the only off-diagonal elements we need. Consider then, instead of (12), the off-diagonal element

$$\langle a\mathbf{k}|\,e^{i(H_A+K)s}e^{-i(H_A+K+V)s}|\,b\mathbf{k}'\rangle. \quad (23)$$

One may use integral equation (13) again, and write it in the form

$$\langle a\mathbf{k}|\,b\mathbf{k}'\rangle-i\int_0^s dt\, e^{i(E_a+\epsilon)t}\langle a\mathbf{k}|\,Ve^{-i(H_A+K+V)t}|\,b\mathbf{k}'\rangle. \quad (24)$$

Then, one may reason as before that $e^{-i(H_A+K+V)t}|b\mathbf{k}'\rangle$ is equivalent to $e^{-i(E_b+\epsilon')t}|\psi_{b\mathbf{k}'}{}^+\rangle$ for large t, and that for large s one may replace (24) by

$$\langle a\mathbf{k}|b\mathbf{k}'\rangle - i\int_0^s dt\, e^{i(E_a+\epsilon)t}\langle a\mathbf{k}|V|\psi_{b\mathbf{k}'}{}^+\rangle e^{-i(E_b+\epsilon')t}. \quad (25)$$

The argument is not as clear cut as before, because the integrand is an oscillatory function and the result could possibly be very small. However, it is correct for the only matrix elements we need to consider, where the energy difference is much smaller than τ^{-1}. In order to see this, we use Eq. (16) again (applied to $|b\mathbf{k}'\rangle$) and we note that (25) would be exactly correct if we added to $\langle a\mathbf{k}|V|\psi_{b\mathbf{k}'}{}^+\rangle$ the quantity

$$-\sum_c \int \frac{d^3k''}{8\pi^3} \frac{\langle a\mathbf{k}|V|\psi_{c\mathbf{k}''}\rangle\langle\psi_{c\mathbf{k}''}|V|b\mathbf{k}'\rangle}{E_b+\epsilon'-E_c-\epsilon''+i\eta} \times e^{i(E_b+\epsilon'-E_c-\epsilon'')t}. \quad (26)$$

We recall that the collision time can also be defined as the relative rate of variation with energy of a matrix element such as $\langle a\mathbf{k}|V|\psi_{c\mathbf{k}''}\rangle$ as $\mathbf{k}''$ is varied away from the energy shell (see Sec. 8 of I). Therefore, if t is much larger than both collision times, most of the variation of the integrand in (26) is due to the exponential and the denominator, and one may as a first approximation consider the matrix elements as constant while one integrates over the length of $\mathbf{k}''$. But then the integral vanishes, because of the relation, valid for $t>0$,

$$\int_\infty^{+\infty} (\omega+i\eta)^{-1}e^{i\omega t}d\omega = 0. \quad (27)$$

Thus, the corrective term (26) is certainly very small. Since, in addition, the period of oscillation of the integrand in (25) is very large compared to the collision time, (25) is a good approximation to (23) when s is much larger than τ. But if, instead of using integral equation (13) when evaluating (23), we had used another equivalent equation, namely

$$e^{-i(H_A+K+V)s} = e^{-i(H_A+K)s} - i\int_0^s dt\, e^{-i(H_A+K+V)(s-t)}Ve^{-i(H_A+K)t}, \quad (28)$$

we could have shown, by a similar chain of arguments, that a good approximation to (23) is

$$\langle a\mathbf{k}|b\mathbf{k}'\rangle - i\int_0^s dt\, e^{i(E_a+\epsilon)t}\langle\psi_{a\mathbf{k}}{}^-|V|b\mathbf{k}'\rangle e^{-i(E_b+\epsilon')t}, \quad (29)$$

where $\langle\psi_{a\mathbf{k}}{}^-|$ is a scattering wave function with ingoing scattered waves. This looks different from (25). But it is well known[8] that the two matrix elements $\langle a\mathbf{k}|V|\psi_{b\mathbf{k}'}{}^+\rangle$ and $\langle\psi_{a\mathbf{k}}{}^-|V|b\mathbf{k}'\rangle$ are equal on the energy shell. Off the energy shell, they differ. But their rate of variation as one goes away from the energy shell is given by the collision time, and we have said that we were not interested in going off the energy shell as far as τ^{-1}. Hence, for our purpose, the two matrices are practically equal and we shall designate them by a common notation, R,

$$\langle a\mathbf{k}|R|b\mathbf{k}'\rangle \simeq \langle a\mathbf{k}|V|\psi_{b\mathbf{k}'}{}^+\rangle \simeq \langle\psi_{a\mathbf{k}}{}^-|V|b\mathbf{k}'\rangle. \quad (30)$$

This slight uncertainty should not be considered as a defect of the theory. It is part of the impact approximation and the error thus made is of the same order of magnitude as other corrections to the impact approximation. For nonoverlapping lines, we need only the diagonal elements and this feature does not arise.

It follows from the validity conditions which we shall give shortly that the interesting values of s are indeed much larger than the collision time. Then, we have shown that each factor in the product (10) may be replaced by the operator

$$\mathcal{U} - i\int_0^s dt\, e^{i(H_A+K)t}Re^{-i(H_A+K)t}. \quad (31)$$

As we expected, this is very closely related to the scattering matrix. With the same normalization, the scattering matrix is[8]

$$S = \mathcal{U} - 2\pi i\delta(E-E')R = \mathcal{U} - i\int_{-\infty}^{+\infty} dt\, e^{i(H_A+K)t}Re^{-i(H_A+K)t}. \quad (32)$$

When the impact approximation is valid and the collisions are disentangled, the operator (10) itself is a time-ordered product of N factors like (31). We shall now use this to compute the line shape, given by (7). For ρ we substitute the unperturbed density matrix, $Z^{-1}\exp[-\beta(H_A+\sum K_j)]$. A discussion of this will follow presently. Since Z^{-1} is independent of s, it affects only the absolute intensity in the spectrum, not the shape, and we shall not concern ourselves with it. Then the operator $\exp(i\sum K_j s)T(s)\rho$ which occurs in (7) is equal to the operator (8) or (10) multiplied by $e^{-iH_A s}$ on the left and by $\exp[-\beta(H_A+\sum K_j)]$ on the right. We shall first multiply each factor (31) by $e^{-\beta K}$, after which we can take the trace over the perturber coordinates, which we denote by Tr_p. Then we have N factors of the following kind:

$$\mathcal{U}\,\mathrm{Tr}_p e^{-\beta K} - i\int_0^s dt\,\mathrm{Tr}_p e^{i(H_A+K)t}Re^{-i(H_A+K)t}e^{-\beta K}. \quad (33)$$

We shall divide through by $\mathcal{U}$, in order to return to the correct normalization. We define an average R, R_{Av}, involving only the atomic coordinates, by the relation

$$R_{Av}\,\mathrm{Tr}_p e^{-\beta K} = \mathrm{Tr}_p e^{-\beta K}R, \quad (34)$$

or

$$\langle a|R_{Av}|b\rangle \sum_k e^{-\beta\epsilon}=\sum_k e^{-\beta\epsilon}\langle a\mathbf{k}|R|b\mathbf{k}\rangle. \quad (35)$$

We drop from (33) the factor $\mathrm{Tr}_p e^{-\beta K}$, which may be considered as canceling part of Z^{-1}. Thus, each of our N factors is

$$1-i\mathcal{U}^{-1}\int_0^s dt\, e^{iH_At}R_{Av}e^{-iH_At}=1-i\mathcal{U}^{-1}\int_0^s dt\, R_{Av}'(t). \quad (36)$$

The ordered product of N factors equal to (36) is

$$\mathfrak{T}\exp\left[-in\int_0^s R_{Av}'(t)dt\right], \quad (37)$$

where n is the perturber density, $n=N/\mathcal{U}$. We define a non-Hermitian operator $\mathfrak{C}$ by

$$\mathfrak{C}=nR_{Av}. \quad (38)$$

When (37) is multiplied to the left by e^{-iH_As}, we obtain (by showing the identity of the derivatives)

$$\exp[-i(H_A+\mathfrak{C})s]. \quad (39)$$

We now have $\Phi(s)$ written in terms of operators involving only the atom,

$$\Phi(s)=\mathrm{Tr}_A\{D\exp[-i(H_A+\mathfrak{C})s]\rho_A\}, \quad (40)$$

and this expression is identical with the classical impact result, as given by (II, 13) and (II, 30). From now on, we can follow the method of II to calculate the line shape. The results for an isolated line will be given in Sec. 4.

We are now ready to state some precise validity conditions. In order that expression (10) be disentangled for most Feynman diagrams, it is necessary that the average collision be weak and that the time interval between strong collisions be much larger than τ. Thus it takes, on the average, a time much larger than τ before the atom feels appreciably disturbed. Since the average effect of the collisions upon the atom can be measured by the width w and the shift d of the levels, we require

$$w\tau\ll 1, \quad (41a)$$

$$d\tau\ll 1. \quad (41b)$$

Those are the same conditions we had in II. By virtue of the relation (72c) between the width and the cross section, condition (41a) can also be written

$$U\ll n^{-1}, \quad (42)$$

which is the same condition we had in I. But there was nothing in I analogous to condition (41b). This was due to the particularly simple type of additivity of the forces that was assumed there. In general, it is true that the impact approximation is valid and the line has a Lorentz shape whenever (41a) is valid. But, unless (41b) is valid too, $\mathfrak{C}$ is not given by (38) and (30), but things are more complicated. Since the case where (41a) is valid while (41b) is not rarely occurs in practice, we shall not go into this question here. We recall that τ can never be smaller than ϵ^{-1}, ϵ being the energy of one of the perturbers, including the inelastically scattered ones. Hence we have the following conditions as consequences of (41)

$$w\ll\epsilon, \quad (43a)$$

$$d\ll\epsilon. \quad (43b)$$

Finally, we shall justify our use of the free density matrix, $\exp[-\beta(H_A+\sum K_j)]$, instead of $\exp[-\beta(H_A+\sum K_j+\sum V_j)]$. This follows from the fact that strong collisions occur rarely and that the perturbers are free most of the time. Since the time between interactions is so large that we can make the scattering approximation, i.e., we stay on the energy shell or almost on the energy shell, the density matrix is the same after the interaction as before and we do not run into the trouble of a time-dependent density matrix as happens sometimes in nonimpact cases. We must keep in mind that the energy of the perturbers is of order β^{-1} and that the collision time cannot be smaller than ϵ^{-1}, thus β is a lower limit for the collision time. It follows from (41a) that the variation of $\beta\omega$ over the width of a line is always very small and that the problem of correcting the shape of a line for the Boltzmann factor should never arise *when the impact approximation is valid*. This result is a consequence of quantum mechanics and does not come out of the classical path theory. One may put it in another way: if $\beta\omega$ varies appreciably over the width of a line, it is an indication that the impact approximation breaks down through quantum-mechanical effects.[10]

The above argument can also be stated analytically. If we want to include the correct density matrix, we must consider the operator $\exp(i\sum K_j s)T(s)\rho$ in (7) all at once. For this, we replace s by $s-i\beta$ in (8) and therefore also in (10) and (11). One convinces oneself easily, using the fact $\beta<\tau$, that equations such as (15) and (25) are still true when s is much larger than τ, provided one replaces s in those equations by $s-i\beta$. Therefore we end up with (37), but with s replaced by $s-i\beta$. However, since the validity conditions tell us that $\beta\mathfrak{C}$ is negligible, everything turns out as though we had used the unperturbed density matrix.

3. THE TWO-STATE CASE

We shall now consider the case where both the initial and final states of the atomic line interact with the perturbers. Again, we start from (3) and our object is to perform the trace over the perturber coordinates first; this reduces $\Phi(s)$ to the classical expression of II.

[10] A similar conclusion was reached by P. W. Anderson, Phys. Rev. **76**, 471 (1949).

We shall rewrite (3) in the form

$$\Phi(s)=\mathrm{Tr}[\mathbf{d}T^*(s)\exp(-i\sum K_j s)\mathbf{d}\exp(i\sum K_j s)T(s)\rho]. \quad (44)$$

As in Sec. 6 of II, we shall "double" the atom, and designate by subscripts i and f operators that act on the initial and final components of a line, respectively. As long as we are only summing over the perturber coordinates, we do not need to bother with the dipole operators. Thus, the expression which we wish to compute is

$$\mathrm{Tr}_p[T_f^*(s)\exp(-i\sum K_j s)][\exp(i\sum K_j s)T_i(s)\rho_i]. \quad (45)$$

This expression contains two complete sets of atomic coordinates, but only one kind of perturber coordinates. Any operator having i as a subscript and independent of the perturber coordinates commutes with any operator having subscript f and independent of the perturber coordinates. But those operators that act on the perturbers have to be kept in the right order. For the density matrix ρ_i we shall use again the product of $\exp(-\beta\sum_j K)$ by a purely atomic factor, and we shall assume as we did in II that this atomic factor does not vary appreciably over the width of a line, or of a group of overlapping lines, and hence can be considered as constant.

The method will consist in using the work of Sec. 2 to evaluate each of the two factors in (45). Again, the impact approximation is the case where the strong collisions are disentangled. The weak collisions may be shown to lead to no entanglement, by an argument similar to that of Sec. 4 of II. We may distinguish two collision times, one for the initial states and one for the final states. The larger of the two will be called τ and will be referred to, simply, as the collision time. The impact approximation is the case where the collisions take, on the average, a time much longer than τ to disturb the line appreciably. Hence the important values for s are much larger than τ and the validity conditions are still (41), w and d being the line width and shift, respectively.

An important practical problem is the electron broadening of a line emitted by an ion. In this case, the interaction of an electron with both the initial state and the final state of the ion includes the Coulomb potential. It was pointed out in Sec. 10 of I that it is impossible, then, to define a collision time, because the potential is too long-ranged. But it is only the difference between the interactions in the initial and final states that is effective in broadening the line and therefore it should be possible for the impact approximation to be valid in this case too. Indeed, such was the case for the simplified theory of I. In order to include such a possibility in the present theory, we shall assume that the operator K may contain a potential, independent of the internal coordinates of the atom and common to both initial and final states. This potential takes care of that part of the elastic scattering which is common to both states. If the elastic scattering is not particularly important, then this potential is not necessary. But it insures that the results of I are obtained when there is only elastic scattering. For reasons of economy of notations, we shall not write this potential explicitly, but shall just imagine that it has been added to K and subtracted from V. The eigenfunctions of K will not be plane waves any more, but scattering functions with outgoing or ingoing scattered waves, which we shall designate by $\phi_{\mathbf{k}}^+$ or $\phi_{\mathbf{k}}^-$. The collision time and the collision volume are then defined (very roughly) as the time during which, or the volume inside which, the wave function differs appreciably from an eigenfunction of K, instead of a plane wave, and they will always be finite. The results of Sec. 2 which we shall need will have to be slightly modified to allow for this extra potential. For instance, we must replace the plane waves by the functions $\phi_{\mathbf{k}}$ in the definitions (20) and (22) of U and σ.

Consider a matrix element of the second factor in the trace (45), forgetting about the density matrix which is already taken care of,

$$\langle\phi_{\mathbf{k}_1'}^-\phi_{\mathbf{k}_2'}^-\cdots\phi_{\mathbf{k}_N'}^-|\exp(i\sum K_j s)T_i(s)|\times\phi_{\mathbf{k}_1}^+\phi_{\mathbf{k}_2}^+\cdots\phi_{\mathbf{k}_N}^+\rangle. \quad (46)$$

We are taking the matrix element only with respect to the perturber coordinates. The above expression is still an operator as far as the atomic coordinates are concerned. We shall use many matrix elements of that type in what follows. When the impact approximation is valid, the work of Sec. 2 (slightly modified) tells us that (46) is equal to $e^{-iH_{Ai}s}$ times an ordered product of N disentangled factors, each of which is

$$\langle\phi_{\mathbf{k}'}^-|\phi_{\mathbf{k}}^+\rangle - i\int_0^s dt\, e^{i(H_{Ai}+\epsilon')t}\langle\phi_{\mathbf{k}'}^-|R_i|\phi_{\mathbf{k}}^+\rangle e^{-i(H_{Ai}+\epsilon)t}, \quad (47)$$

where the operator R is defined, in the vicinity of the energy shell only, by the relation

$$\langle b\phi_{\mathbf{k}'}^-|R|a\phi_{\mathbf{k}}^+\rangle\simeq\langle b\phi_{\mathbf{k}'}^-|V|\psi_{a\mathbf{k}}^+\rangle\simeq\langle\psi_{b\mathbf{k}'}^-|V|a\phi_{\mathbf{k}}^+\rangle. \quad (48)$$

The last two members of this equation are equal on the energy shell.[8] Similarly, a matrix element of the first factor in (45),

$$\langle\phi_{\mathbf{k}_1}^+\cdots\phi_{\mathbf{k}_N}^+|T_f^*(s)\exp(-i\sum K_j s)|\times\phi_{\mathbf{k}_1'}^-\cdots\phi_{\mathbf{k}_N'}^-\rangle, \quad (49)$$

is equal to an anti-time-ordered product (we are taking the Hermitian conjugate !) of N disentangled factors, times $e^{iH_{Af}s}$. Each factor is

$$\langle\phi_{\mathbf{k}}^+|\phi_{\mathbf{k}'}^-\rangle + i\int_0^s dt'\, e^{i(H_{Af}+\epsilon)t'}\langle\phi_{\mathbf{k}}^+|R_f|\phi_{\mathbf{k}'}^-\rangle e^{-i(H_{Af}+\epsilon')t'}. \quad (50)$$

We must now multiply (46) and (49) together and integrate over all $\mathbf{k}'$s. Since in (45) all operators of (49) act to the left of all operators of (46), it would seem that the operators are not properly ordered any more and that we shall have to disentangle them further. But this is not the case because, as we are going to show, the product of (47) and (50) gives an appreciable contribution only when the two times, t and t', are within a collision time of each other. Since the interval between (strong) collisions is on the average much longer than the collision time, the collisions are indeed disentangled from each other, i.e., we get a vanishing result unless the ordering of the collisions is the same in both (46) and (49). *Thus, the perturbers must arrive in the same order and at approximately the same times for both initial and final states, and we shall be able to deal with the perturbers one at a time, each of them affecting the line in its turn without entanglement.*

To prove the assertion made about the times t and t', we multiply (47) and (50) together and integrate over $\mathbf{k}'$, obtaining (note that $\langle\phi_\mathbf{k}^+|\phi_\mathbf{k}^+\rangle=\mathcal{U}$)

$$\begin{aligned}\mathcal{U}&-i\int_0^s dt\, e^{iH_At}\langle\phi_\mathbf{k}^+|R_i|\phi_\mathbf{k}^+\rangle e^{-iH_At}\\&+i\int_0^s dt'\, e^{iH_Bt'}\langle\phi_\mathbf{k}^+|R_f^*|\phi_\mathbf{k}^+\rangle e^{-iH_Bt'}\\&+\int_0^s dt\int_0^s dt'\int(d^3k'/8\pi^3)e^{i(H_B+\epsilon)t'}\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle\\&\times e^{-i(H_B+\epsilon')t'+i(H_A+\epsilon')t}\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle e^{-i(H_A+\epsilon)t}.\end{aligned}\quad(51)$$

The fourth term can be rewritten in the form

$$\begin{aligned}\int_0^s dt\int_{t-s}^t d(t-t')\int(d^3k'/8\pi^3)&e^{i(H_B+\epsilon)t}\\&\times e^{-i(H_B+\epsilon)(t-t')}\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle e^{i(H_B+\epsilon')(t-t')}\\&\times e^{i(H_A-H_B)t}\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle e^{-i(H_A+\epsilon)t}.\end{aligned}\quad(52)$$

We recall that the collision time gives the rate of variation of the function R as one varies $\mathbf{k}'$ away from the energy shell. If $(t-t')$ is much larger than τ, the exponentials involving $(t-t')$ oscillate many times, as $\mathbf{k}'$ is varied, while R_i and R_f do not change much, hence the integral over $\mathbf{k}'$ is very small. Clearly, it would be possible to construct a rigorous argument along the lines of those of I. Since $(t-t')$ is restricted to a region of order of magnitude τ anyway, we can integrate over it from $-\infty$ to $+\infty$, which gives 2π times a δ function, and (52) becomes

$$\begin{aligned}2\pi\int_0^s dt\, e^{i(H_A+H_B)t}&\int(d^3k'/8\pi^3)\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle\\&\times\delta(E_f-E_f')\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle e^{-i(H_A+H_B)t},\end{aligned}\quad(53)$$

where E_f and E_f' are the total energies of the two states between which R_f^* is taken. But if, instead of integrating over t and $(t-t')$ as in (52), we had chosen to integrate over t' and $(t'-t)$, we would have obtained in like manner

$$\begin{aligned}2\pi\int_0^s dt'\, e^{i(H_A+H_B)t'}&\int(d^3k'/8\pi^3)\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle\\&\times\delta(E_i-E_i')\langle\phi_{\mathbf{k}'}^-|R_j|\phi_\mathbf{k}^+\rangle e^{-i(H_A+H_B)t'},\end{aligned}\quad(54)$$

with a δ function of the energy difference of the two states between which R_i is taken. Fortunately, the two expressions are almost equal, because we are only interested in matrix elements between two lines (i.e., doubled states) whose frequencies differ by much less than τ^{-1}. Let us write out the atomic states explicitly. We have the two matrices $\langle\alpha\phi_\mathbf{k}^+|R_f^*|\beta\phi_{\mathbf{k}'}^-\rangle$ and $\langle b\phi_{\mathbf{k}'}^-|R_i|a\phi_\mathbf{k}^+\rangle$, and in one case we have $\delta(E_\alpha-E_\beta+\epsilon-\epsilon')$, while in the other we have $\delta(E_a-E_b+\epsilon-\epsilon')$. The frequencies of the two lines are E_a-E_α and E_b-E_β. If those are almost equal, E_a-E_b and $E_\alpha-E_\beta$ are also almost equal, q.e.d.

We have thus shown that the product of (47) and (50), integrated over $\mathbf{k}'$, is equal to

$$\mathcal{U}-i\int_0^s dt\, e^{i(H_A+H_B)t}Q(\mathbf{k})e^{-i(H_A+H_B)t},\quad(55)$$

with

$$\begin{aligned}Q(\mathbf{k})=&\langle\phi_\mathbf{k}^+|R_i|\phi_\mathbf{k}^+\rangle-\langle\phi_\mathbf{k}^+|R_f^*|\phi_\mathbf{k}^+\rangle\\&+2\pi i\int(d^3k'/8\pi^3)\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle\\&\times\delta(E-E')\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle.\end{aligned}\quad(56)$$

This begins to resemble closely a product of S matrices. Indeed, the two S matrices are[8] (here as above, E and E' stand for the total energy, atom plus perturber)

$$\begin{aligned}\langle\mathbf{k}'|S_i|\mathbf{k}\rangle=&\langle\phi_{\mathbf{k}'}^-|\phi_\mathbf{k}^+\rangle\\&-2\pi i\delta(E_i-E_i')\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle,\end{aligned}\quad(57)$$

$$\begin{aligned}\langle\mathbf{k}|S_f^*|\mathbf{k}'\rangle=&\langle\phi_\mathbf{k}^+|\phi_{\mathbf{k}'}^-\rangle\\&+2\pi i\delta(E_f-E_f')\langle\phi_\mathbf{k}^+|R_f|\phi_{\mathbf{k}'}^-\rangle.\end{aligned}\quad(58)$$

In these equations, each term is still an operator acting on the atomic coordinates. The first term on the right-hand side is not the unit operator, but an S matrix of its own, representing the scattering by K alone. The product of the two S matrices is

$$\begin{aligned}\int&(d^3k'/8\pi^3)\langle\mathbf{k}|S_f^*|\mathbf{k}'\rangle\langle\mathbf{k}'|S_i|\mathbf{k}\rangle\\&=\mathcal{U}-2\pi i\delta(E_i-E_i')\langle\phi_\mathbf{k}^+|R_i|\phi_\mathbf{k}^+\rangle\\&\quad+2\pi i\delta(E_f-E_f')\langle\phi_\mathbf{k}^+|R_f^*|\phi_\mathbf{k}^+\rangle\\&\quad+4\pi^2\delta(E_i+E_f'-E_i'-E_f)\\&\quad\times\int(d^3k'/8\pi^3)\langle\phi_\mathbf{k}^+|R_f^*|\phi_{\mathbf{k}'}^-\rangle\\&\qquad\times\delta(E-E')\langle\phi_{\mathbf{k}'}^-|R_i|\phi_\mathbf{k}^+\rangle\\&=\mathcal{U}-i\int_{-\infty}^{+\infty}dt\, e^{i(H_A+H_B)t}Q(\mathbf{k})e^{-i(H_A+H_B)t}.\end{aligned}\quad(59)$$

The analogy with (55) is clear. But the S matrix can also be expressed in terms of the true transition amplitude, T, which describes the complete scattering, including that part due to K alone, as follows[8]

$$\langle \mathbf{k}'|S_i|\mathbf{k}\rangle=\langle \mathbf{k}'|\mathbf{k}\rangle-2\pi i\delta(E_i-E_i')\langle \mathbf{k}'|T_i|\mathbf{k}\rangle, \quad (60)$$

$$\langle \mathbf{k}|S_f^*|\mathbf{k}'\rangle=\langle \mathbf{k}|\mathbf{k}'\rangle+2\pi i\delta(E_f-E_f')\langle \mathbf{k}|T_f^*|\mathbf{k}'\rangle. \quad (61)$$

Note that the first term on the right-hand side is now the unit operator. It is possible, then, to express Q in terms of T, in the following way:

$$Q(\mathbf{k})=\langle \mathbf{k}|T_i|\mathbf{k}\rangle-\langle \mathbf{k}|T_f^*|\mathbf{k}\rangle$$

$$+2\pi i\int (d^3k'/8\pi^3)\langle \mathbf{k}|T_f^*|\mathbf{k}'\rangle\delta(E-E')\langle \mathbf{k}'|T_i|\mathbf{k}\rangle. \quad (62)$$

This may sometimes be more convenient than the expression in terms of R, since T involves the complete scattering amplitudes and cross sections, while R has been truncated by the subtraction of a potential from V.

In order to obtain (45), we must still multiply (55) by $e^{-\beta\epsilon}$ and integrate over $\mathbf{k}$, then raise it to the Nth power, keeping the ordering correct, multiply to the left by $e^{-iH_{Ai}s}$ and to the right by $e^{iH_{Af}s}$, and finally include the atomic density matrix ρ_A. We define an average Q by the relation

$$\sum_{\mathbf{k}} e^{-\beta\epsilon}Q(\mathbf{k})=Q_{\mathrm{Av}}\sum_{\mathbf{k}} e^{-\beta\epsilon}, \quad (63)$$

and we shall agree not to write $\sum_{\mathbf{k}} e^{-\beta\epsilon}$, but to consider it as canceling part of Z^{-1}. As in Sec. 6 of II, we shall transpose all operators bearing the subscript f. This changes the anti-time-ordering to time-ordering, the same as for the i operators. As in II, we use the superscript $+$ to denote the straight complex conjugate of an operator, which is the transpose of the Hermitian conjugate. The result of this transposition applied to Q_{Av} we call $\bar{Q}_{\mathrm{Av}}$. We divide (55) by $\mathcal{V}$ to reinstate the correct normalization. Then, after the average over $\mathbf{k}$ and the transposition, it becomes

$$1-i\mathcal{V}^{-1}\int_0^s dt\,\bar{Q}_{\mathrm{Av}}'(t), \quad (64)$$

with

$$\bar{Q}_{\mathrm{Av}}'(t)=\exp[i(H_{Ai}-H_{Af}{}^+)t]\bar{Q}_{\mathrm{Av}}\times\exp[-i(H_{Ai}-H_{Af}{}^+)t]. \quad (64a)$$

The perturber coordinates have now been completely eliminated. Then we raise to the Nth power, with the proper ordering, and obtain

$$\mathfrak{T}\exp\left\{-in\int_0^s dt\,\bar{Q}_{\mathrm{Av}}'(t)\right\}. \quad (65)$$

Finally, we multiply to the left by $e^{-iH_{Ai}s}$ and by $\exp(iH_{Af}{}^+s)$ (also to the left, since we have transposed). The result is (for the usual reason)

$$\exp[-i(H_{Ai}-H_{Af}{}^++\mathfrak{K})s], \quad (66)$$

with

$$\mathfrak{K}=n\bar{Q}_{\mathrm{Av}}. \quad (67)$$

The connection with II has now been acheived. With the definition (II, 56) of Δ, we can write $\Phi(s)$, (44), in the form of a trace over the atomic coordinates (in line space) only,

$$\Phi(s)=\mathrm{Tr}_A\{\Delta\exp[-i(H_{Ai}-H_{Af}{}^++\mathfrak{K})s]\rho_A\}, \quad (68)$$

which is identical with the classical result, as given by (II, 58) and (II, 60).

One more remark might be in order here. We have shown that, when the impact approximation is valid, we can express the spectrum in terms of the transition matrices near the energy shell, i.e., in terms of the various scattering amplitudes. But we have implied throughout this work that the perturbers could be distinguished from the particles inside the atom. If the perturbers are electrons, this is not the case, and the true scattering amplitudes involve exchange effects. Indeed, these true scattering amplitudes are the ones that must be used in the pressure broadening calculation. In other words, from every amplitude computed for distinguishable particles we must subtract one or several exchange amplitudes, to take into account the fact that the perturbing electron may remain inside the atom and one of the original atomic electrons may be expelled in its place.

4. SHIFT AND WIDTH OF AN ISOLATED LINE[11]

From now on, one can follow the work of II to compute the line shape. This involves inverting the matrix $(\omega-H_{Ai}+H_{Af}{}^+-\mathfrak{K})$, the number of lines and columns of the matrix being equal to the number of spectral lines that overlap. Then the line shape, $F(\omega)$, is given by Eq. (II, 62)

$$F(\omega)=-\pi^{-1}\rho\mathcal{J}\,\mathrm{Tr}[\Delta(\omega-H_{Ai}+H_{Af}{}^+-\mathfrak{K})^{-1}], \quad (69)$$

where ρ has been considered as constant for that particular group of lines. The only difference from II is that $\mathfrak{K}$ is given by the quantum-mechanical expressions (67), (63), (62), or (56), instead of the classical expression (II, 61). In the one-state case, $\mathfrak{K}$ is given by (38), (34), and (30).

The case of an isolated line is that where $\mathfrak{K}$ is small compared to the level spacing of the unperturbed Hamiltonian, and therefore can be treated by first-order perturbation theory. In the one-state case, as we saw in Sec. 5 of II, the shift is just the real part ($\mathcal{R}$) of the diagonal element of $\mathfrak{K}$, while the width is the negative of its imaginary part ($\mathcal{J}$). Thus, in the one-

[11] The results derived in this section were presented at the 1957 annual meeting of the American Physical Society [M. Baranger, Bull. Am. Phys. Soc. Ser. II, 2, 54 (1957)].

state case, for the atomic level a,

$$\text{Shift}=d=n\mathcal{R}\langle a\mathbf{k}|R|a\mathbf{k}\rangle_{\text{Av}}, \tag{70a}$$

$$\text{Width}=w=-n\mathcal{I}\langle a\mathbf{k}|R|a\mathbf{k}\rangle_{\text{Av}}. \tag{70b}$$

We assume here that the atomic level is nondegenerate. The degenerate case is considered at the end of this section. The matrix elements of R on the energy shell are proportional to the scattering amplitudes. Calling $\mathbf{k}'$ a vector whose length is the same as that of $\mathbf{k}$ but which makes angles θ and φ with it, we have the relation analogous to (I, 35):

$$\langle a\mathbf{k}'|R|a\mathbf{k}\rangle=-(2\pi/m)f(\theta,\varphi), \tag{71}$$

where f is the elastic scattering amplitude of a perturber of momentum $\mathbf{k}$ by an atom in state a. Therefore the shift and width are simply proportional to the real and imaginary parts of the forward elastic scattering amplitude,

$$d=-(2\pi n/m)\mathcal{R}[f(0)]_{\text{Av}}, \tag{72a}$$

$$w=(2\pi n/m)\mathcal{I}[f(0)]_{\text{Av}}. \tag{72b}$$

These relations are the same as (I, 36). Here again, we can use the optical theorem which relates the imaginary part of the forward elastic scattering amplitude to the total cross section (elastic plus inelastic) σ,

$$\mathcal{I}f(0)=(k/4\pi)\sigma. \tag{73}$$

Then the width is given in terms of σ by the same relation as (I, 36c):

$$w=(\tfrac{1}{2}nv\sigma)_{\text{Av}}. \tag{72c}$$

One can also express the shift and width in terms of phase shifts, but since there can be inelastic collisions the phase shifts have to be complex. Equation (I, 41) for the scattering amplitude still holds, but with complex δ_l. Instead of talking about complex phase shifts, one may replace $e^{2i\delta_l}$ by $\alpha_l e^{2i\delta_l}$, with δ_l real and α_l real and smaller than one. Then Eqs. (I, 42) have to be replaced by

$$d=-[(\pi n/mk)\textstyle\sum_l(2l+1)\alpha_l\sin 2\delta_l]_{\text{Av}}, \tag{74a}$$

$$w=[(\pi n/mk)\textstyle\sum_l(2l+1)(1-\alpha_l\cos 2\delta_l)]_{\text{Av}}. \tag{74b}$$

These equations constitute the natural quantum-mechanical generalization of the classical equations (II, 53). They apply only to a nondegenerate atomic state.

The effect of inelastic collisions on an isolated line may be viewed in the following manner. A perturber comes along and induces a transition in the atom from state a to a different state b. Then, later, another perturber collides and induces another transition. It may happen that this second transition returns the atom to state a. But so much time elapses between the two collisions and the frequencies of a and b are so different that the phase of the atom after it has returned to a will be completely unrelated to what the phase would have been if the atom had stayed in a all the time. Thus, the effect is equivalent to a complete interruption of the radiation and contributes a width, proportional to the inelastic cross section, but no shift. On the other hand, it may happen that the frequency of b is so close to that of a that the two phases do not have time, in the interval between the two collisions, to differ by more than a small angle. Then, we have a case of overlapping lines and, then, the effect of the inelastic collisions between the two states a and b is not as simple as a mere interruption of radiation, but it has a coherent contribution as well. This is why the theory of overlapping lines is more complicated than that of isolated lines.

Now, let us consider the two-state case. The matrix elements of the transition operator T on the energy shell are related to the two elastic scattering amplitudes, f_i and f_f, in a manner analogous to Eq. (71):

$$\langle a\mathbf{k}'|T_i|a\mathbf{k}\rangle=-(2\pi/m)f_i(\theta,\varphi), \tag{75a}$$

$$\langle\alpha\mathbf{k}'|T_f|\alpha\mathbf{k}\rangle=-(2\pi/m)f_f(\theta,\varphi). \tag{75b}$$

We are assuming that $|a\rangle$ and $|\alpha\rangle$ are nondegenerate, i.e., their angular momentum, if it exists, must be zero. This restriction will be removed later. The shift and width of an isolated line are given as in Sec. 6 of II by the real part and the negative of the imaginary part, respectively, of the diagonal element of $\mathfrak{IC}$ in line space. We express $\mathfrak{IC}$ in terms of T, and we perform the integration over the δ function in (62) by writing

$$d^3k'=mk'd\epsilon'd\Omega, \tag{76}$$

where $d\Omega$ is the element of solid angle. The result is

$$d=\Big\{-(2\pi n/m)\mathcal{R}[f_i(0)-f_f(0)] + \tfrac{1}{2}inv\int d\Omega[f_f^*(\Omega)f_i(\Omega)-f_f(\Omega)f_i^*(\Omega)]\Big\}_{\text{Av}}, \tag{77a}$$

$$w=\Big\{(2\pi n/m)\mathcal{I}[f_i(0)+f_f(0)] - \tfrac{1}{2}nv\int d\Omega[f_f^*(\Omega)f_i(\Omega)+f_f(\Omega)f_i^*(\Omega)]\Big\}_{\text{Av}}. \tag{77b}$$

The average is taken over all energies and angles of the perturber, with the Boltzmann weighting factor $e^{-\beta\epsilon}$. Again, these expressions are identical with those arising in Sec. 6 of I. The width can be transformed by the optical theorem (73). The total cross section σ is the sum of the inelastic cross section, σ_{in}, and the elastic cross section,

$$\sigma=\sigma_{\text{in}}+\int d\Omega|f(\Omega)|^2. \tag{78}$$

Therefore, the width becomes

$$w=\left\{\tfrac{1}{2}nv\left[\sigma_{i\text{ in}}+\sigma_{f\text{ in}}+\int d\Omega|f_i(\Omega)-f_f(\Omega)|^2\right]\right\}_{\text{Av}}, \quad (77c)$$

which differs from the pure-elastic result (I, 53b) by the occurrence of the inelastic cross sections. The fact that the shift (77a) is identical with the shift (I, 53a) of the pure-elastic theory should not surprise us, since the addition of inelastic collisions cannot be expected to change the frequency of the light, but only to interrupt emission more often. The fact that the width differs from the pure-elastic width by the two inelastic cross sections is also normal, since the effects of inelastic collisions cannot be expected to add coherently. But it would be a grave mistake to believe that the width should involve the sum of the two *total* cross sections. The elastic parts of the scattering subtract in a coherent manner, and it is the difference between the two elastic scattering amplitudes that counts. It is easy to write the shift and width in terms of phase shifts and to derive expressions generalizing (I, 56) and (II, 72).

Finally, we shall consider an isolated line between two levels $|a\rangle$ and $|\alpha\rangle$ whose angular momenta j_a and j_α do not vanish. The considerations of Sec. 7 of II must be used to take the rotational degeneracy into account. The result obtained there was that we should replace $\mathfrak{K}$ by a matrix in "reduced line space," h, given by (II, 84), and then proceed as in the case of no degeneracy. This procedure is easily applied to the present calculation of the shift and width. Each elastic scattering amplitude now becomes a $(2j+1)\times(2j+1)$ matrix, $\langle m_a'|f_i(\theta,\varphi)|m_a\rangle$ and $\langle m_\alpha'|f_f(\theta,\varphi)|m_\alpha\rangle$, where m is the magnetic quantum number before scattering and m' afterwards. According to (II, 84), we must replace the expression $f_f^*f_i\pm f_ff_i^*$ which occurs in (77a, b) by

$$\sum_{\mu m_a m_a' m_\alpha m_\alpha'}\langle j_\alpha m_\alpha'|\mu^*|j_a m_a'\rangle\langle m_a'|f_i|m_a\rangle \times\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle\langle m_\alpha|f_f^*|m_\alpha'\rangle \pm\text{complex conjugate}, \quad (79)$$

with the definitions

$$\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle=(2j_a+1)^{-\frac{1}{2}}C(j_\alpha 1 j_a;\, m_\alpha\mu m_a) =\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle, \quad (80)$$

where C is a Clebsch-Gordan coefficient in the notation of Rose.[12] Similarly, we must replace $|f_i-f_f|^2$ in (77c) by

$$\sum_{\mu m_a' m_\alpha}\Big|\sum_{m_a}\langle m_a'|f_i|m_a\rangle\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle -\sum_{m_\alpha'}\langle j_a m_a'|\mu|j_\alpha m_\alpha'\rangle\langle m_\alpha'|f_f|m_\alpha\rangle\Big|^2. \quad (81)$$

Finally, according to (II, 84), (II, 80), and (II, 81), we replace $f_i(0)$ and $f_f(0)$ in (77a, b), and $\sigma_{i\text{ in}}$ and $\sigma_{f\text{ in}}$ in (77c), by

$$(2j_a+1)^{-1}\textstyle\sum_{m_a}\langle m_a|f_i(0)|m_a\rangle, \quad (82a)$$

$$(2j_\alpha+1)^{-1}\textstyle\sum_{m_\alpha}\langle m_\alpha|f_f(0)|m_\alpha\rangle, \quad (82b)$$

$$(2j_a+1)^{-1}\textstyle\sum_{m_a}\langle m_a|\sigma_{i\text{ in}}|m_a\rangle, \quad (83a)$$

$$(2j_\alpha+1)^{-1}\textstyle\sum_{m_\alpha}\langle m_\alpha|\sigma_{f\text{ in}}|m_\alpha\rangle, \quad (83b)$$

respectively. Once these changes are made, the shift and width are given correctly by Eqs. (77). In other words, whenever a scattering amplitude or a cross section appears singly in Eqs. (77), one replaces it by an average over magnetic quantum numbers of the diagonal elements. But where a product of scattering amplitudes occurs, one must use the more complicated type of average (79) or (81), which involves Clebsch-Gordan coefficients. The rule is the same in the one-state case, when the angular momentum j_a does not vanish. One must replace $f(0)$ and σ in (72) by averages over magnetic quantum numbers, as in (82) and (83).

[12] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley and Sons, Inc., New York, 1957).