Problem of Overlapping Lines in the Theory of Pressure Broadening

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The theory of pressure broadening is re-examined, in order to include the possibility of overlapping lines, which are a regular feature of pressure broadening in an ionized gas. It is found that a simple treatment can be given using the impact approximation. This approximation is examined in detail, and its validity conditions are discussed. When it is valid, it is permissible to replace the exact time-dependent interaction between the atom and the perturbers by a time-independent effective interaction. The latter is not Hermitian, however, and therefore every level acquires a width. The shape of a group of overlapping lines is then worked out, and is found to consist of a sum of Lorentz line shapes, plus some interference terms. In the particular case of an isolated line, the results given previously by Anderson are obtained. Finally, a study is made of the simplifications brought about by rotational invariance.

1. INTRODUCTION

THE problem of overlapping lines arises naturally when one tries to compute the pressure broadening in an ionized gas. The free electrons and the ions in the gas disturb the atom that is emitting the light. The effect of the ions can usually be taken into account by the theory of Holtsmark,[1] or static theory, or Stark broadening theory. According to this theory, the electric field of the ions splits the line through the Stark effect. The resulting pattern is then averaged over all electric fields with the appropriate probability distribution. The electrons, on the other hand, move too fast to be treated in this way. But the impact theory[2] is usually valid for them.[3] In order to take into account ions and electrons simultaneously, the procedure must be, therefore, to apply the impact theory to the electrons when a certain ionic field is present, then to average the result over ionic fields. Since the effect of the ionic field is usually to split the line into a number of components, we are faced with the problem of applying the impact theory to a number of very close lines, which, when broadened by the electrons, will overlap.

Overlapping lines also arise occasionally in other pressure broadening problems, of course, but they have not been considered in any of the theoretical treatments. The most complete study of the impact theory is that of Anderson,[4] and it is restricted to isolated lines. The most up-to-date treatment of hydrogen line shapes in ionized gases is that of Kolb,[5] but his work had to stay incomplete because of this difficulty. Kolb's results are restricted to the wings of the lines, where the overlapping problem does not arise. It is obviously desirable to extend the theory to the core of the lines, which is the most characteristic and interesting part.

In this paper, we shall generalize the impact theory to make it applicable to overlapping lines. Thus, this work is an extension of the work of Anderson,[4] and we shall obtain Anderson's results again in the particular case of an isolated line. Like Anderson, we make the impact approximation. This consists essentially in assuming that the average collision is weak, although it does not preclude the possibility of a few strong collisions.[6] But the time interval between the strong collisions is much larger than their duration. This is the approximation which results in an isolated line having a Lorentz shape. It is discussed thoroughly, and the conditions for its validity are investigated, in Secs. 3 and 4. It turns out to be very often valid for electrons in ionized gases. We shall assume, in addition, that the perturbers[7] move completely independently of each other, without mutual interactions. In the case of an ionized gas, we may have to correct this later to take into account mutual screening of the perturbers beyond the Debye radius. We shall put no restriction on the nature of the interaction between the perturbers and the atom. The collisions may be inelastic as well as elastic.

The main result of this study is the following: when the impact approximation is valid, it is possible to replace the fluctuating, time-dependent interaction between the atom and the perturbers by a constant effective interaction, $\mathcal{K}$. We might call $\mathcal{K}$ the average interaction, but it is not just equal to the time-average of the true interaction. It is not Hermitian, and is related to the collision matrix, as we shall see in Secs. 3 and 6. The spectrum of the light emitted is the same as

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[1] J. Holtsmark, Ann. Physik **58**, 577 (1919); Physik. Z. **20**, 162 (1919); **25**, 73 (1924). [See also the following reviews of pressure broadening theory: 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] E. Lindholm, Arkiv Mat. Astron. Fysik **28B**, No. 3 (1941); H. M. Foley, Phys. Rev. **69**, 616 (1946); P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[3] M. Baranger, Phys. Rev. **91**, 436(A) (1953).

[4] P. W. Anderson, reference 2.

[5] Alan C. Kolb, "Theory of Hydrogen Line Broadening in High-Temperature Partially Ionized Gases," University of Michigan Engineering Research Institute, ASTIA Document No. AD 115 040 (unpublished).

[6] By "weak" and "strong" collisions we mean those which result in a small (compared to unity) and large change in the wave function of the light-emitting atom, respectively.

[7] The name "perturbers" will be used, from now on, to designate the particles that cause the line broadening. We shall always call the particle that is emitting the light "the atom," although it may be an ion or a molecule.

if the Hamiltonian of the atom were the sum of its unperturbed Hamiltonian and $\mathcal{H}$. Since $\mathcal{H}$ is not Hermitian, the eigenvalues of the Hamiltonian are complex and an isolated line has a Lorentz shape. The shape of a group of overlapping lines is worked out in Secs. 5 and 6.

This paper contains no applications of the theory. Work is now in progress on the shape of hydrogen lines in an ionized gas, and will be reported later. In another paper, to be published soon, we shall show how the motion of the perturbers can be treated quantum mechanically, with little modification of the basic results. In the present work, the perturbers are assumed to follow classical paths.

2. THE SPECTRUM

In this section, we shall derive general formal expressions for the spectral distribution of the light emitted. We shall be very brief, since these expressions have already been given by Anderson.[4] We neglect the natural line width, which, in practice, is usually much smaller than pressure broadening effects. The perturbers are assumed to move on given classical paths, and their motion is not influenced by what happens to the atom. Thus, their contribution to the Hamiltonian of the atom is a given time-dependent function. This neglect of the reaction of the atom upon the perturbers is the source of some theoretical difficulties (see later in this section), but seems justified in practice. The paths of the perturbers are usually taken to be straight lines, for convenience, but this is not necessary.

The first step must be to write down a formula giving the intensity of the light emitted or absorbed by a quantum-mechanical system with an arbitrary time-dependent Hamiltonian. Such a formula is a straightforward consequence of the principles of quantum electrodynamics and has already appeared in the literature many times.[8] If we call $P(\omega)d\omega$ the power emitted or absorbed in frequency interval $d\omega$ about ω, we have

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

$$F(\omega)=(2\pi T)^{-1}\left|\int_0^T dt e^{i\omega t}\langle\psi_f(t)\,|\,\mathbf{d}\,|\,\psi_i(t)\rangle\right|^2. \tag{2}$$

In this equation, $\psi_i(t)$ is the initial state and $\psi_f(t)$ the final state of the system, in the Schrödinger picture. Positive ω's correspond to emission, negative ω's to absorption. The same two initial and final states may give rise to both emission and absorption, a phenomenon which is usually important only for very low frequencies. c is the speed of light. n_+ is the number of photons per quantum state after the emission or before the absorption, i.e., for whichever state of the radiation field has the larger number of photons. n_+ is unity for spontaneous emission. For absorption or induced emission, n_+ is connected to the intensity of the light beam in the well-known manner.[9] $\mathbf{d}$ is the vector electric dipole moment of the system, in the Schrödinger picture, i.e., time-independent. We are considering only electric dipole radiation. The absolute square in (2) also involves a summation over the three components of $\mathbf{d}$. Equation (1) has already been summed over all angles and polarizations of the light. Finally, T is a very large time, which in the limit should be taken infinite. In the following, $F(\omega)$ will be called "the spectrum," or, in case of an individual line, "the line shape." This is slightly incorrect, but convenient. The true line shape contains in addition the factor $(4\omega^4 n_+/3c^3)$.

The observed spectrum is obtained by summing (2) over all final states, averaging over all initial states, and averaging over all possible types of motion of the perturbers. We denote this latter average by the subscript Av. We denote by ρ_i the probability of a given initial state (the density matrix). Thus, the complete spectrum can be written

$$F(\omega)=(2\pi T)^{-1}\int_0^T dt\int_0^T dt' e^{i\omega(t-t')}\Phi(t,t'), \tag{3}$$

with

$$\Phi(t,t')=\sum_{if}\rho_i[\langle\psi_i(t')\,|\,\mathbf{d}\,|\,\psi_f(t')\rangle\cdot\langle\psi_f(t)\,|\,\mathbf{d}\,|\,\psi_i(t)\rangle]_{\text{Av}}. \tag{4}$$

It is not essential to sum over *all* initial and final states. If a line is isolated, one obtains the shape of this line alone by omitting the summation in (4), and picking the appropriate initial and final states. But if several lines overlap, we *must* sum at least over all initial and final states that contribute to the overlapping lines.

The next step consists in saying that $\Phi(t,t')$ depends only on the time difference $t-t'$. This is evident since, after the average over all types of perturber motion has been performed, there is nothing to distinguish one time from another in the behavior of the system. Hence we can choose t and $t-t'=s$ as new integration variables. The integral over t is trivial, and just cancels the factor T^{-1} in front. The integral over s can be extended from $-\infty$ to $+\infty$, since it turns out to converge at both ends. In (4), t' can be set equal to 0 and t to s. Therefore, we get

$$F(\omega)=(2\pi)^{-1}\int_{-\infty}^{+\infty} e^{i\omega s}\Phi(s)ds, \tag{5}$$

with

$$\Phi(s)=\sum_{if}\rho_i[\langle\psi_i(0)\,|\,\mathbf{d}\,|\,\psi_f(0)\rangle\cdot\langle\psi_f(s)\,|\,\mathbf{d}\,|\,\psi_i(s)\rangle]_{\text{Av}}. \tag{6}$$

The quantity $\Phi(s)$ is what Anderson[4] calls the "correlation function." It is also the Fourier transform of the spectrum. It always turns out to be easier to compute the Fourier transform of the spectrum than the spec-

[8] P. W. Anderson, reference 2; S. Bloom and H. Margenau, Phys. Rev. **90**, 791 (1953).

[9] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1944), second edition, Sec. 11.

trum itself. To make $F(\omega)$ real, we must have

$$\Phi(-s)=[\Phi(s)]^*, \tag{7}$$

where the asterisk means complex conjugate. This is easily seen to follow from (4). Therefore we shall always be content to calculate $\Phi(s)$ for positive s, and for negative s we shall use (7). Alternatively, one can write

$$F(\omega)=\pi^{-1}\Re\int_0^\infty e^{i\omega s}\Phi(s)ds, \tag{8}$$

where $\Re$ means the real part.

We can modify (6) by introducing the Schrödinger evolution operator, $T(s)$, which transforms a state at time 0 into a state at time s,

$$T(s)|\psi(0)\rangle=|\psi(s)\rangle, \tag{9}$$

and which is unitary. Using it and using the density matrix ρ, we can formally perform the summation in (6) and obtain $\Phi(s)$ in the form of a trace,

$$\Phi(s)=\mathrm{Tr}[\mathbf{d}T^*(s)\cdot\mathbf{d}T(s)\rho]_{\mathrm{Av}}. \tag{10}$$

The asterisk on an operator will always mean Hermitian conjugate.

We end this section by mentioning some difficulties which result from our neglect of the reaction of the atom upon the perturbers. When we said that (4) depended only on $t-t'$, we implicitly assumed that the density matrix ρ was the same at all times. In a system in thermal equilibrium, it would be a Boltzmann distribution. This will not happen, however, unless we take into account the change of energy of a perturber in an inelastic collision with the atom. If we neglect this change, the atomic density matrix cannot stay constant, and in fact the atom will eventually reach infinite temperature, with all states equally likely. This is absurd, and therefore we must hope, or verify, that the times s that are important in (5) are not so large that the density matrix has time to change appreciably from the initial Boltzmann distribution. To state the criterion in another way, ρ must be practically time-independent, hence it must commute with the evolution operator $T(s)$. Then, there should be no difference between $\Phi(s)$ as written in (10) and the following:

$$\Phi(s)=\mathrm{Tr}[\mathbf{d}T^*(s)\cdot\mathbf{d}\rho T(s)]_{\mathrm{Av}}. \tag{10a}$$

We shall see that this is actually true with the impact approximation. The same difficulty arises in another manner when one tries to verify that the "principle of detailed balancing" is satisfied. This principle states that, when our system is in thermal equilibrium with radiation, the number of photons of a particular frequency emitted per unit time equals the number absorbed. Bloom and Margenau[10] have pointed out that this may not be true with the assumption of predetermined classical paths. Again, the trouble does not arise when the impact approximation is valid.

[10] S. Bloom and H. Margenau, reference 8.

3. THE IMPACT APPROXIMATION

In this and the next two sections, we shall consider the case where we can neglect the interaction of the perturbers with the lower state of the atom. We call it the one-state case. This case is easier of physical interpretation than the general case or two-state case. Besides, it arises often in practice, since the atom is more tightly bound and less polarizable in its lower state. We shall consider the case of emission, i.e., the lower state is the final state.

The problem is to compute $\Phi(s)$, given by (6) or (10). We shall introduce the final state explicitly, since we do not need to sum over all final states. On the other hand, since we are interested in overlapping lines, we must sum over initial states. Thus, we start from[11]

$$\Phi(s)=\mathrm{Tr}\sum_\alpha[\mathbf{d}|\psi_{f\alpha}\rangle e^{iE_fs}\cdot\langle\psi_{f\alpha}|\mathbf{d}T(s)\rho]_{\mathrm{Av}}. \tag{11}$$

We have introduced a degeneracy index, α, for the final state, on which we must sum if the final state is degenerate. E_f, the energy of the final state, will be taken as the origin of energies. Thus, we replace e^{iE_fs} by unity. We define a Hermitian operator D by

$$D=\sum_\alpha\mathbf{d}|\psi_{f\alpha}\rangle\cdot\langle\psi_{f\alpha}|\mathbf{d}. \tag{12}$$

If j, m, and parity are good quantum numbers for the final state, D is a spherically symmetric operator, i.e., it can have matrix elements only between two states with the same j, m, and parity. With these conventions, $\Phi(s)$ becomes

$$\Phi(s)=\mathrm{Tr}[DT_{\mathrm{Av}}(s)\rho]. \tag{13}$$

The problem, now, is to evaluate the average of $T(s)$.

$T(s)$ is the evolution operator for the total Hamiltonian, which is the sum of H_0, the unperturbed atomic Hamiltonian, and $V_T(t)$, the total interaction. It obeys the Schrödinger equation

$$idT/ds=[H_0+V_T(s)]T(s). \tag{14}$$

One can also define an interaction representation evolution operator, $U(s)$, by the equation

$$T(s)=e^{-iH_0s}U(s). \tag{15}$$

Then, it is well known that $U(s)$ can be written

$$U(s)=\mathfrak{T}\exp\left[-i\int_0^s V_T'(t)dt\right], \tag{16}$$

with

$$V_T'(t)=e^{iH_0t}V_T(t)e^{-iH_0t}. \tag{17}$$

In the above, $\mathfrak{T}$ is the time-ordering operator, which makes operators act in the order prescribed by the time in their argument, with time increasing from right to

[11] We assume that the units are such that $\hbar=1$, and hence we make no distinction between an energy and an angular frequency.

left. Equation (16) can be proved by checking that $T(s)$, given by (15), actually obeys the differential equation (14).

The interaction $V_T'(t)$ is a sum of interactions, $V_1'(t)$, $V_2'(t)$, $\cdots V_N'(t)$ due to the various perturbers. Thus we may write

$$U(s)=\mathfrak{T}\exp\left[-i\int^s V_1'(t)dt\right]\cdots \times\exp\left[-i\int_0^s V_N'(t)dt\right], \quad (18)$$

and

$$U_{Av}(s)=\mathfrak{T}\left\{\left[\exp\left(-i\int_0^s V'(t)dt\right)\right]_{Av}\right\}^N, \quad (19)$$

N being the total number of perturbers in the container. We have expressed $U_{Av}(s)$ in the form of the Nth power of an expression relating to a single perturber. It then bears a striking resemblance to the result of the simpler theory which uses the adiabatic approximation. This result is[12]

$$\Phi(s)=\left\{\left[\exp\left(-i\int_0^s V(t)dt\right)\right]_{Av}\right\}^N. \quad (20)$$

However (19) is enormously more complex than (20), first because the expression whose Nth power we are taking is an operator, second because the operation $\mathfrak{T}$ produces a hopeless entanglement[13] of the operators, out of which it would be very difficult to extricate any simple result in the general case.

At this point, we make the impact assumption. It says that two strong collisions never occur simultaneously. Then, the operators in (19) are "naturally disentangled," i.e., the collisions take place one after the other and the order in which the operators are written in (18) is also the order required by time-ordering. Really, it is only the strong collisions that are separated from each other. There may be several weak collisions going on at the same time, or together with one strong collision. But those can be treated by perturbation theory, because they are weak, hence they never get entangled with each other, because it is only in the higher orders that entanglement starts to appear. A discussion of this point, and some validity conditions, will be given in the next section.

Assuming no entanglement, then, we can compute $U_{Av}(s)$ by computing first an expression relating to a single perturber,

$$\left[\mathfrak{T}\exp\left(-i\int_0^s V'(t)dt\right)\right]_{Av}, \quad (21)$$

then raising it to the Nth power, while keeping the collisions in chronological order. Let us try now to calculate (21), by averaging over all possible states of motion of the perturber. From the validity conditions which will be given in the next section, one can conclude that the important values for s are much larger than a typical collision time. This is because the average collision is weak, hence it takes many collisions to produce a $U_{Av}(s)$ appreciably different from unity. In the overwhelming majority of situations, the bracket in (21) equals unity, because the perturber does not make any collision in the time interval 0 to s. Once in a great while, a collision occurs in this time interval. The probability of this happening is of order N^{-1}. The probability of two collisions occurring is of order N^{-2}, and can be neglected. We consider all possible types of collision, i.e., all possible values for the impact parameter, energy of the perturber, angles, etc. We call $d\nu$ the frequency of a particular type of collision when all the perturbers are present. Then, the frequency with a single perturber is $N^{-1}d\nu$, and the probability of such a collision occurring in time dt is $N^{-1}d\nu dt$. We talk about the collision as if it occurred instantaneously, since s is much larger than the collision time. If a collision occurs at time t between 0 and s, the bracket of (21), instead of being unity, equals

$$e^{iH_0t}Se^{-iH_0t}, \quad (22)$$

where S is the collision matrix, or S-matrix, for a collision occurring at time 0. S is a unitary matrix given by

$$S=\mathfrak{T}\exp\left[-i\int_{-\infty}^{+\infty} V'(t)dt\right], \quad (23)$$

for a collision whose time of closest approach is 0. It is clear that, if a collision does not occur at time 0, its result is (22) and not S itself, since the atomic state at time t is really e^{-iH_0t} times what it was at time 0. Finally, the deviation from unity in (21) due to a collision of a given type occurring in time interval dt at time t is

$$N^{-1}d\nu dt(e^{iH_0t}Se^{-iH_0t}-1). \quad (24)$$

We obtain (21) by considering all types of collision and all times between 0 and s. Therefore (21) is equal to

$$1+N^{-1}\int_0^s dte^{iH_0t}\left[\int(S-1)d\nu\right]e^{-iH_0t}. \quad (25)$$

This may be written

$$1-iN^{-1}\int_0^s \mathcal{H}'(t)dt, \quad (26)$$

with

$$\mathcal{H}'(t)=e^{iH_0t}\mathcal{H}e^{-iH_0t}, \quad (27)$$

[12] P. W. Anderson, Phys. Rev. **86**, 809 (1952).
[13] R. P. Feynman, Phys. Rev. **84**, 108 (1951).

and

$$\mathcal{K}=-i\int(1-S)d\nu. \tag{28}$$

To obtain $U_{Av}(s)$ we raise (26) to the Nth power, with the proper time-ordering, thus:

$$U_{Av}(s)=\mathfrak{T}\exp\left[-i\int_0^s \mathcal{K}'(t)dt\right]. \tag{29}$$

Then, $T_{Av}(s)$ is obtained by (15):

$$\begin{aligned}T_{Av}(s)&=e^{-iH_0 s}\mathfrak{T}\exp\left[-i\int_0^s \mathcal{K}'(t)dt\right]\\&=\exp[-i(H_0+\mathcal{K})s].\end{aligned} \tag{30}$$

This last equation can be proved by showing the identity of the derivatives with respect to s.[13a]

We have thus shown that, when the impact approximation is valid, it is permissible to replace the true time-dependent interaction $V_T(t)$ by a time-independent quantity, $\mathcal{K}$, given by (28). Since $\mathcal{K}$ is not Hermitian, the energy levels have an imaginary part, i.e., a width. To compute $\mathcal{K}$, we must know the collision matrix S. The calculation of S is a standard problem in time-dependent quantum mechanics. It may be a very difficult one. Fortunately, $\mathcal{K}$ is not very sensitive to the details of S, since it involves a sum over all types of collision, and we can hope that a rather crude approximation to S will yield a rather good $\mathcal{K}$. We refer the reader to Anderson's paper[4] for approximate methods of calculation of S. As a first approximation, we can divide all collisions into two categories, weak ones and strong ones. For the weak ones, we compute S by time-dependent perturbation theory. For the strong ones, we say that the radiation is completely interrupted, i.e., we replace S by zero. Further refining may be necessary to properly take into account collisions of intermediate strength. It may also turn out, especially for close collisions, that it is necessary to treat the motion of the perturbers quantum mechanically when calculating S. This can be done, in principle, and will be the subject of a future publication. In general, it may be objected that our approximation of predetermined classical paths is a very bad one to use when calculating matrix elements of $\mathcal{K}$, or S, between two states of widely different energy. The answer is that we do not need such matrix elements. The only matrix elements we shall need are either on the energy shell or close to it.

The determination of the line shape, using Eqs. (13) and (30), will be given in Sec. 5. Now, we shall return to the question of the validity of the approximation.

[13a] Equations (13) and (30) bear a close formal resemblance to some results obtained in a rather different connection by P. W. Anderson, J. Phys. Soc. Japan 9, 316 (1954). I am indebted to Dr. Anderson for pointing out this analogy.

4. VALIDITY CONDITIONS

Starting from (16), we can write

$$U_{Av}(s+\Delta s)=\left\{\mathfrak{T}\exp\left[-i\int_s^{s+\Delta s} V_T'(t)dt\right]\times\mathfrak{T}\exp\left[-i\int_0^s V_T'(t)dt\right]\right\}_{Av}. \tag{31}$$

The impact approximation is valid if it is possible to find Δs such that (1) Δs is so large that the first factor on the right-hand side of (31) is statistically independent of the second factor, and the two may be averaged separately; and (2) Δs is so small that the average of the first factor is very close to unity, and may be written

$$1-ie^{iH_0 s}\mathcal{K}e^{-iH_0 s}\Delta s. \tag{32}$$

If these two conditions are satisfied, (31) may be written

$$U_{Av}(s+\Delta s)=(1-ie^{iH_0 s}\mathcal{K}e^{-iH_0 s}\Delta s)U_{Av}(s), \tag{33}$$

or

$$dU_{Av}(s)/ds=-ie^{iH_0 s}\mathcal{K}e^{-iH_0 s}U_{Av}(s), \tag{34}$$

a differential equation whose solution is (29), and the impact approximation is valid. In order to satisfy the first condition, Δs must be taken much larger than a typical collision time. By this we mean the collision time of a collision which makes an appreciable contribution to the integral (28) giving $\mathcal{K}$. If Δs is so large, there will be many collisions in the interval Δs. However, because of the second condition on Δs, most of these collisions will be very weak. There can be at most one strong collision in the interval and most of the time there will be none.

Let us first consider the case where there is no strong collision in the interval Δs. We can write the first factor on the right-hand side of (31) as

$$\mathfrak{T}\exp\left[-i\int_s^{s+\Delta s} V_1'(t)dt\right]\times\exp\left[-i\int_s^{s+\Delta s} V_2'(t)dt\right]\cdots, \tag{35}$$

including all the collisions that take place in the interval. The collisions in this expression are entangled. However, let us forget about that for a moment, and compute (35) as if they were not entangled. Since each collision is very weak, the contribution from each of them is very close to 1. The first collision contributes $1+M_1$, the second $1+M_2$, etc., where M_1, M_2, $\cdots$ are very small matrices. When we multiply all these expressions together, we get

$$1+(M_1+M_2+\cdots)+\text{higher-order terms such as } M_1M_2. \tag{35a}$$

However, because the product (35) is required to be very close to 1 still, the higher-order terms are negligible compared to the first-order term, $(M_1+M_2+\cdots)$. If now we try to take the entanglement into account in the calculation of (35), we see that (35a) is still correct except for the fact that the higher-order terms are now different. But since those are negligible, the result is the same, whether there is entanglement or not. Since the average number of collisions of a given type in interval Δs is $\Delta s d\nu$, this result is, after the averaging,

$$1+\Delta s\int M d\nu = 1+\Delta s e^{iH_0 s}\left[\int (S-1)d\nu\right]e^{-iH_0 s}. \quad (36)$$

By comparing (32) and (36), we see that $\mathfrak{IC}$ is indeed given by (28).

We now consider the rare case where there is one strong collision in the interval Δs. This collision is so much stronger than the others that we can forget about all the others in computing (35), at least during the collision time of the strong collision. Thus, the question of entanglement does not arise here and (36) still holds.

Thus, we have shown that the impact approximation is valid, and the interaction may be replaced by a time-independent $\mathfrak{IC}$, whenever $U_{Av}(t)$ is very close to unity for times of the order of a typical collision time τ. Another way to put it is as follows. Call T the time that it takes for $U_{Av}(t)$ to become appreciably different from unity. We require $T\gg\tau$. An order of magnitude for T is given by the inverse of the correction introduced by $\mathfrak{IC}$ in the eigenvalues of the Hamiltonian, i.e., the inverse of the level width w, or of the level shift d, whichever is greater. Hence, we can write the following validity conditions[14]:

$$w\ll\tau^{-1}, \quad (37a)$$

$$d\ll\tau^{-1}. \quad (37b)$$

We shall mention here, because we shall use them later, the additional validity conditions which one finds[14a] when the motion of the perturbers is treated quantum mechanically. They are

$$w\ll\epsilon, \quad (38a)$$

$$d\ll\epsilon, \quad (38b)$$

where ϵ is the energy of the perturbers. If, in a certain problem, (38) is not satisfied, while (37) is, it is an indication that the impact approximation breaks down through quantum-mechanical effects.

Let us end this section by giving two examples of the validity conditions (37). First, suppose that the forces between the atom and the perturbers vary smoothly with distance, as forces between atoms and molecules usually do (long-range forces). Then w and d are of the same order of magnitude. We may estimate the collision time by saying that $v\tau$ (v is the velocity) must be of order of magnitude $\sigma^{-\frac{1}{2}}$, where σ is the "classical cross section," defined by

$$w=nv\sigma, \quad (39)$$

and n is the average perturber density. Then the validity condition is

$$\sigma^{\frac{1}{2}}\ll n^{-1}, \quad (40)$$

or "the radius of the cross-section disk must be much smaller than the average nearest neighbor distance." Another way of saying the same thing is "the S matrix for an average nearest neighbor collision must be very close to unity." The other example is the case where the strength of the forces is approximately constant with distance until a certain range a, after which it drops sharply (finite-range forces). Then $v\tau$ is of order a, and both w and d must turn out much smaller than v/a.

5. THE LINE SHAPE IN THE ONE-STATE CASE

The Fourier transform of the line shape is given by (13) and (30). The density matrix ρ should be proportional to $\exp(-H_0/kT)$, where k is Boltzmann's constant and T the temperature. As we pointed out at the end of Sec. 2, we must check that this effectively commutes with $T_{Av}(s)$ for the important values of s. This is a consequence of conditions (38) which require that the shift and width of the levels be much smaller than the energy of the perturbers, and therefore than kT. Then, ρ varies too slowly with energy to affect the shape of the individual lines, and we can consider it as a constant for each line or group of a few lines.

The line shape itself is obtained from (8). We may perform the integral with $T_{Av}(s)$ in the operator form (30). The imaginary parts of the eigenvalues of $H_0+\mathfrak{IC}$ are of the right sign to make the integral convergent at infinity. We obtain (ρ is a constant)

$$\pi\rho^{-1}F(w)=-\mathcal{I}\,\mathrm{Tr}[D(\omega-H_0-\mathfrak{IC})^{-1}], \quad (41)$$

where $\mathcal{I}$ means the imaginary part. At this point we introduce the eigenstates of $H_0+\mathfrak{IC}$, $|\varphi_i\rangle$, and the eigenvalues, ω_i-iw_i ($w_i>0$):

$$(H_0+\mathfrak{IC})|\varphi_i\rangle=(\omega_i-iw_i)|\varphi_i\rangle. \quad (42)$$

Since $H_0+\mathfrak{IC}$ is not Hermitian, the states $|\varphi_i\rangle$ are not mutually orthogonal. But we can define another set of states, $\langle\chi_j|$, such that

$$\langle\chi_j|\varphi_i\rangle=\delta_{ij}, \quad (43)$$

and therefore

$$\textstyle\sum_i|\varphi_i\rangle\langle\chi_i|=1. \quad (44)$$

[14] These validity conditions are really not the most general ones. But they are sufficient in most cases, and we did not feel justified in going into the more general discussion necessary to treat the subject completely. Actually, the impact approximation is valid and the interaction can be replaced by something time-independent whenever (37a) is true, even if (37b) is not. This may happen, for instance, if the total interaction is due to a large number of perturbers at all times. Then, the time-average of the interaction constitutes the main part of the correction to H_0, and the levels are shifted much more than they are widened. In this case (28) has to be somewhat modified unless (37b) holds.

[14a] Work to be published.

Then (41) can be written

$$\pi\rho^{-1}F(\omega)$$
$$=-\mathcal{g}\sum_i\langle\chi_i|D(\omega-H_0-\mathfrak{IC})^{-1}|\varphi_i\rangle$$
$$=-\mathcal{g}\sum_i(\omega-\omega_i+iw_i)^{-1}\langle\chi_i|D|\varphi_i\rangle$$
$$=\sum_i\left[\frac{w_i}{(\omega-\omega_i)^2+w_i^2}\mathcal{R}\langle\chi_i|D|\varphi_i\rangle\right.$$
$$\left.-\frac{\omega-\omega_i}{(\omega-\omega_i)^2+w_i^2}\mathcal{g}\langle\chi_i|D|\varphi_i\rangle\right]. \quad (45)$$

One sees that the shape of a group of overlapping lines is not composed solely of a sum of Lorentz line shapes, but there are also some asymmetrical terms. For large ω, each of these terms becomes proportional to ω^{-1}. In order that the total intensity be convergent, the sum of their coefficients must vanish. This is indeed the case since this sum is $-\mathcal{g}\,\mathrm{Tr}D$, and the trace of a Hermitian operator is real. Hence, the asymmetrical terms are important only in a region of overlapping lines.[14b]

It is possible to transform (41) to a different form which also shows the nonexistence of terms proportional to ω^{-1}. We write

$$\pi\rho^{-1}F(\omega)$$
$$=(2i)^{-1}\,\mathrm{Tr}\{D[(\omega-H_0-\mathfrak{IC}^*)^{-1}-(\omega-H_0-\mathfrak{IC})^{-1}]\}$$
$$=(2i)^{-1}\,\mathrm{Tr}\{D[(\omega-H_0-\mathfrak{IC}^*)^{-1}(\omega-H_0-\mathfrak{IC})$$
$$\times(\omega-H_0-\mathfrak{IC})^{-1}-(\omega-H_0-\mathfrak{IC}^*)^{-1}$$
$$\times(\omega-H_0-\mathfrak{IC}^*)(\omega-H_0-\mathfrak{IC})^{-1}]\}$$
$$=-\mathrm{Tr}\{D(\omega-H_0-\mathfrak{IC}^*)^{-1}\mathfrak{IC}^a(\omega-H_0-\mathfrak{IC})^{-1}\}, \quad (46)$$

where $\mathfrak{IC}^a$ is the anti-Hermitian part of $\mathfrak{IC}$. This can also be written in terms of components, like (45). If we are far from any line center, we may forget about the anti-Hermitian part of $\mathfrak{IC}$ in the two reciprocals. And, if we are far, not only with respect to the widths, but also with respect to the shifts, we may also forget about the Hermitian part of $\mathfrak{IC}$, thus getting

$$\pi\rho^{-1}F(\omega)\simeq-\mathrm{Tr}[D(\omega-H_0)^{-1}\mathfrak{IC}^a(\omega-H_0)^{-1}]. \quad (47)$$

Equation (47), for the case where $\mathfrak{IC}^a$ is computed by perturbation theory, has been given by Kolb,[15] in a completely different notation. It is valid only in the wings, while (41) and (46) are valid everywhere. Finally, if we are much farther away from a group of lines than the separation between the lines, we may replace H_0 by some sort of average energy, E_0, and write

$$\pi\rho^{-1}F(\omega)\simeq-(\omega-E_0)^{-2}\,\mathrm{Tr}(D\mathfrak{IC}^a). \quad (48)$$

[14b] The purpose of the preceding argument is to bring out the general analytical form (45) of the line shape. However, for an actual calculation of the line, it is usually not convenient to solve the eigenvalue equation (42). It is easier to calculate the trace (41) directly in the representation where H_0 is diagonal. The number of lines and columns in each matrix should be the number of overlapping lines, hence the calculation of the reciprocal presents no problem in simple cases. The same remark applies also to Sec. 6.

[15] Reference 5, p. 63.

Even if the lines appear to be well separated, this may be very different from what one would get by adding together the individual Lorentz functions for the individual lines.

We shall now show how the results of the no-overlap theory of Anderson[4] are obtained. We restrict ourselves here to nondegenerate levels. Anderson also considered degenerate levels in great detail. We whall investigate them in Sec. 7. To get Anderson's results, it must be permissible to compute the eigenvalues of $H_0+\mathfrak{IC}$ by first-order perturbation theory. Thus, if $|\psi_i\rangle$ and E_i are the eigenstates and eigenvalues of H_0, we take

$$\omega_i-iw_i=E_i+\langle\psi_i|\mathfrak{IC}|\psi_i\rangle, \quad (49)$$

and we use the states $|\psi_i\rangle$ instead of $|\varphi_i\rangle$ and $|\chi_i\rangle$. We see then that the second term in (45) vanishes, since a diagonal matrix element of D is real, and the spectrum is (with the density matrix reinstated in the summation)

$$\pi F(\omega)=\sum_i\rho_i\frac{w_i}{(\omega-E_i-d_i)^2+w_i^2}\langle\psi_i|D|\psi_i\rangle, \quad (50)$$

with

$$d_i=\mathcal{R}\langle\psi_i|\mathfrak{IC}|\psi_i\rangle, \quad (51a)$$
$$w_i=-\mathcal{g}\langle\psi_i|\mathfrak{IC}|\psi_i\rangle. \quad (51b)$$

Since we have used perturbation theory, (50) is valid only when $\mathfrak{IC}$ is small compared to the spacing of the levels of H_0, which restricts it to nonoverlapping lines.

Anderson's results involve only the diagonal elements of $\mathfrak{IC}$, or of the S matrix. We can always write

$$\langle\psi_i|S|\psi_i\rangle=\alpha_ie^{-i\varphi_i}, \quad (52)$$

where φ_i is a real phase shift and α_i a real positive number not larger than unity. By (28), then, the shift and width of line i are given by

$$d_i=\int\alpha_i\sin\varphi_i d\nu, \quad (53a)$$

$$w_i=\int(1-\alpha_i\cos\varphi_i)d\nu. \quad (53b)$$

If all collisions are elastic, α_i is unity and one obtains a well known result of Lindholm.[2] If all collisions either are completely inelastic ($\alpha_i=0$), or have a very large φ_i, the shift vanishes and the width equals the collision frequency. This is the Lorentz[16] theory.

6. THE TWO-STATE CASE

Let us now return to the general case, where both the initial and final atomic states interact appreciably with the perturbers. Since we may have overlap effects both in the initial and final states, we must use the general formula (10), which we rewrite here in terms of com-

[16] H. A. Lorentz, Proc. Roy. Acad. Sci. (Amsterdam) 8, 591 (1906).

ponents, using Latin letters for initial states and Greek letters for final states,

$$\Phi(s)=\sum_{abc\alpha\beta}[\langle a|\mathbf{d}|\alpha\rangle\langle\alpha|T^*(s)|\beta\rangle\cdot\langle\beta|\mathbf{d}|b\rangle \times\langle b|T(s)|c\rangle\langle c|\rho|a\rangle]_{Av}. \quad (54)$$

We can make this two-state case very similar to the one-state case of the last three sections by using a stratagem which we shall call "doubling." It consists in considering a new function space which is the direct product of the function space of the atom by itself. In other words, each state of the "doubled" system is associated with two states of the atom or, more precisely, with an initial state and the complex conjugate of a final state. We take the Hamiltonian of the doubled system to be such that its eigenvalue, for each state, is the difference between the two eigenvalues for the two atomic states of which it is formed. Thus, each *eigenvalue* of the doubled system corresponds to a *line* of the atom, i.e., the difference between two energies. Therefore, we shall call the doubled space "line space."

We define three operators in line space, Θ, Δ, and ρ, by the relations

$$\langle\alpha|T^*(s)|\beta\rangle\langle b|T(s)|c\rangle=\langle\langle b\beta^+|\Theta(s)|c\alpha^+\rangle\rangle, \quad (55)$$

$$\langle a|\mathbf{d}|\alpha\rangle\cdot\langle\beta|\mathbf{d}|b\rangle=\langle\langle a\alpha^+|\Delta|b\beta^+\rangle\rangle, \quad (56)$$

$$\langle c|\rho|\alpha\rangle\delta_{\alpha\gamma}=\langle\langle c\gamma^+|\rho|a\alpha^+\rangle\rangle. \quad (57)$$

In these definitions, $|\alpha^+\rangle$, $|\beta^+\rangle$, $|\gamma^+\rangle$, are the complex conjugate states of $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, i.e., their components are the complex conjugates of those of $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$. This slight complication is necessary in order to make the newly defined operators linear. Δ is Hermitian. We can now write (54) as

$$\Phi(s)=\mathrm{Tr}[\Delta\Theta_{Av}(s)\rho], \quad (58)$$

which is the same as (13), except for the fact that all operators are in line space. We must evaluate the average of $\Theta(s)$, and we do this in a way completely analogous to the evaluation of the average of $T(s)$ in Sec. 3. We see that we may write

$$\Theta(s)=T_i(s)T_f^+(s), \quad (59)$$

where the subscripts i and f indicate that the operators act on the first and the second, respectively, of the two states that combine to form a line. The superscript $+$ means complex conjugate, and is not to be confused with the Hermitian conjugate superscript $*$. $T_f^+(s)$ is the transpose of $T_f^*(s)$.

We need not repeat the discussion of Sec. 3. The results are the same. When the impact approximation is valid, the average of $\Theta(s)$ is given by

$$\Theta_{Av}(s)=\exp[-i(H_{0i}-H_{0f}^+ +\mathfrak{K})s], \quad (60)$$

with

$$\mathfrak{K}=-i\int(1-S_iS_f^+)d\nu. \quad (61)$$

$\mathfrak{K}$ is an operator in line space which cannot be decomposed into the sum or the product of operators acting on subspaces i and f separately. The matrices S_i and S_f are given by (23). The argument of Sec. 4 shows that the conditions for validity of the approximation are again (37), where d and w are the real part and the negative of the imaginary part, respectively, of the change in line energy produced by $\mathfrak{K}$, and τ is a typical collision time, i.e., the time during which the interactions of the perturber with the initial and final atomic states are appreciably different, for a collision that makes a significant contribution to $\mathfrak{K}$. As for the density matrix, we shall assume that it does not vary appreciably over the range of initial energies that enter in a given group of overlapping lines, and therefore we shall consider it as a constant.

The argument of Sec. 5 also carries through here. The line shape is given by

$$\pi\rho^{-1}F(\omega)=-\mathcal{I}\,\mathrm{Tr}[\Delta(\omega-H_{0i}+H_{0f}^+-\mathfrak{K})^{-1}] \quad (62)$$

$$=-\mathrm{Tr}[\Delta(\omega-H_{0i}+H_{0f}^+-\mathfrak{K}^*)^{-1} \times\mathfrak{K}^a(\omega-H_{0i}+H_{0f}^+-\mathfrak{K})^{-1}]. \quad (63)$$

We can also write this in terms of components, by introducing the eigenstates and the eigenvalues of $H_{0i}-H_{0f}^+ +\mathfrak{K}$,

$$(H_{0i}-H_{0f}^+ +\mathfrak{K})|\varphi_i\rangle\rangle=(\omega_i-iw_i)|\varphi_i\rangle\rangle, \quad (64)$$

and the states $\langle\langle\chi_j|$ such that

$$\langle\langle\chi_j|\varphi_i\rangle\rangle=\delta_{ij}. \quad (65)$$

Then, we can show as before that

$$\pi\rho^{-1}F(\omega)=\sum_i\left[\frac{w_i}{(\omega-\omega_i)^2+w_i^2}\mathcal{R}\langle\langle\chi_i|\Delta|\varphi_i\rangle\rangle -\frac{\omega-\omega_i}{(\omega-\omega_i)^2+w_i^2}\mathcal{I}\langle\langle\chi_i|\Delta|\varphi_i\rangle\rangle\right], \quad (66)$$

and we can make the same remark about the behavior of the asymmetrical terms for large ω. Far away in the wings, (63) reduces to

$$\pi\rho^{-1}F(\omega)\simeq-\mathrm{Tr}[\Delta(\omega-H_{0i}+H_{0f}^+)^{-1} \times\mathfrak{K}^a(\omega-H_{0i}+H_{0f}^+)^{-1}]. \quad (67)$$

This last expression has also been given by Kolb,[15] in a completely different notation, for the case of perturbation theory.

Anderson's results[4] for isolated lines (without degeneracy) are obtained when it is permissible to solve the eigenvalue problem (64) by first-order perturbation theory. Then, we use states that are eigenstates of

H_{0i} and H_{0f}^{+}, and the spectrum becomes

$$\pi F(\omega)=\sum_{a\alpha}\rho_a\frac{w_{a\alpha}}{(\omega-E_a+E_\alpha-d_{a\alpha})^2+w_{a\alpha}^2}\times\langle\langle a\alpha^+|\Delta|a\alpha^+\rangle\rangle, \quad (68)$$

with

$$d_{a\alpha}=\Re\langle\langle a\alpha^+|\mathfrak{IC}|a\alpha^+\rangle\rangle, \quad (69a)$$

$$w_{a\alpha}=-\mathcal{g}\langle\langle a\alpha^+|\mathfrak{IC}|a\alpha^+\rangle\rangle, \quad (69b)$$

$$\langle\langle a\alpha^+|\Delta|a\alpha^+\rangle\rangle=|\langle a|\mathbf{d}|\alpha\rangle|^2. \quad (70)$$

Using (61), we can express the shift and width in terms of the collision matrix,

$$d_{a\alpha}=-\mathcal{g}\int\langle\langle a\alpha^+|S_iS_f^+|a\alpha^+\rangle\rangle d\nu$$

$$=-\mathcal{g}\int\langle a|S|a\rangle\langle\alpha|S^*|\alpha\rangle d\nu, \quad (71a)$$

$$w_{a\alpha}=\Re\int\langle\langle a\alpha^+|1-S_iS_f^+|a\alpha^+\rangle\rangle d\nu$$

$$=\int(1-\Re\langle a|S|a\rangle\langle\alpha|S^*|\alpha\rangle)d\nu. \quad (71b)$$

If we call $\alpha_ie^{-i\varphi_i}$ and $\alpha_fe^{-i\varphi_f}$ the diagonal elements of S, as in (52), the shift and width become

$$d=\int\alpha_i\alpha_f\sin(\varphi_i-\varphi_f)d\nu, \quad (72a)$$

$$w=\int[1-\alpha_i\alpha_f\cos(\varphi_i-\varphi_f)]d\nu. \quad (72b)$$

Again, these equations include as special cases the results of the adiabatic theory of Lindholm[2] and of the Lorentz[16] theory.

7. SIMPLIFICATIONS DUE TO SPHERICAL SYMMETRY

In many problems the unperturbed Hamiltonian H_0 is spherically symmetric and the effect of the collisions is also spherically symmetric, i.e., there is no preferential direction for the velocities of the perturbers. This spherical symmetry enables one to make some important simplifications in the answers that we have obtained. Anderson[4] did this for his theory of isolated lines, and we shall do it in this section for the more general case.

We shall consider first the one-state case, which is rather trivial. We have already pointed out that D, Eq. (12), is a spherically symmetric operator, i.e., it can have matrix elements only between states of the same j, m, and parity. If the collisions happen in a spherically symmetric manner, the same is true of $\mathfrak{IC}$, Eq. (28). Hence, in the right side of (41) all operators are spherically symmetric, and we can split the spectrum into a sum of spectra belonging to different values of the quantum number j and of parity. In other words, two overlapping levels with different parities or j values may be treated as nonoverlapping. The eigenvalue problem for $H_0+\mathfrak{IC}$ becomes simplified in the way customary for spherically symmetric perturbations.

There is one additional point concerning the calculation of $\mathfrak{IC}$ by (28). Since we know that $\mathfrak{IC}$ is going to be spherically symmetric, it is useless to compute the matrix elements of S between states of different j values or parities. They will disappear anyway in the integral over all types of collision. As to the matrix elements between states of the same j and parity, it is not necessary to calculate them for all possible orientations of a collision. It is sufficient to pick a particularly simple orientation, for instance, impact vector in the z direction, perturber path in the x direction. Those are what Anderson calls the "collision axes." Then, in order to average over all directions, instead of rotating the perturber, we rotate the coordinate axes. The result of this is to average over m the matrix elements between states of the same m, and it is 0 for the other matrix elements. In other words, $\mathfrak{IC}$ is given by the following equation (the subscript p is the parity),

$$\langle am_a|\mathfrak{IC}|bm_b\rangle=-i\delta_{j_aj_b}\delta_{m_am_b}\delta_{p_ap_b}\times\int d\nu[\delta_{ab}-(2j+1)^{-1}\textstyle\sum_m\langle am|S_c|bm\rangle], \quad (73)$$

where S_c is the matrix S computed with the collision axes.

Now, we shall take up the two-state cases, which is the really interesting one. It is still true, of course, that Δ and $\mathfrak{IC}$ are spherically symmetric, but spherical symmetry in line space is an unusual notion which needs some explanation. First, it is well known that the matrix elements of the dipole moment are, as far as their dependence on the magnetic quantum numbers goes, proportional to certain Clebsch-Gordan coefficients.[17] Instead of d_x, d_y, d_z, we shall use

$$d_0=d_z, \quad d_1=(d_x+id_y)/\sqrt{2}, \quad d_{-1}=(d_x-id_y)/\sqrt{2}, \quad (74)$$

as components of the dipole moment, and instead of (see Sec. 6)

$$\langle a|\mathbf{d}|\alpha\rangle\cdot\langle\beta|\mathbf{d}|b\rangle,$$

we shall write

$$\sum_{\mu=-1,0,1}\langle a|d_\mu|\alpha\rangle\langle\beta|d_\mu^*|b\rangle. \quad (75)$$

The proportionality relation that we just stated will

[17] This is the Wigner-Eckart theorem. [See M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley and Sons, Inc., New York, 1957), p. 85.]

be written

$$\langle am_a|d_\mu|\alpha m_\alpha\rangle=(a|d|\alpha)\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle, \quad (76)$$

where $(a|d|\alpha)$ is independent of m_a, m_α, and μ, and

$$\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle=(2j_a+1)^{-\frac{1}{2}}C(j_\alpha 1 j_a; m_\alpha \mu m_a). \quad (77)$$

C is a Clebsch-Gordan coefficient in the notation of Rose.[17] It is real. The complex conjugate of relations (76) and (77) are

$$\langle \alpha m_\alpha|d_\mu^*|am_a\rangle=(\alpha|d^*|a)\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle, \quad (78)$$

$$\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle=(2j_a+1)^{-\frac{1}{2}}C(j_\alpha 1 j_a; m_\alpha \mu m_a). \quad (79)$$

It follows from the properties of Clebsch-Gordan coefficients that

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

$$\sum_{\mu m_a}\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle\langle j_a m_a|\mu|j_\alpha m_\alpha'\rangle=(2j_\alpha+1)^{-1}\delta_{m_\alpha m_\alpha'} \quad (81)$$

$$\sum_{\mu m_a m_\alpha}\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle=1. \quad (82)$$

This is all subject to the condition that j_a and j_α differ by no more than one unit. Otherwise, the Clebsch-Gordan coefficients vanish.

According to Anderson, the fact that $\mathcal{H}$ is spherically symmetric has the consequence that we can write

$$\sum_{m_b m_\beta}\langle\langle am_a{}^+m_\alpha\alpha^+|\mathcal{H}|bm_b\beta^+m_\beta{}^+\rangle\rangle\langle j_b m_b|\mu|j_\beta m_\beta\rangle=\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle((a\alpha^+|h|b\beta^+)), \quad (83)$$

where $((a\alpha^+|h|b\beta^+))$ is independent of any magnetic quantum number, including μ. The proof of (83) goes as follows: all we need to show is that both sides of the equation transform in the same way under rotations, since $\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle$ is completely specified by its behavior under rotations. When we do make a rotation, $\mathcal{H}$ in the left-hand side of the equation does not need to be rotated, since it is spherically symmetric. We do not need to rotate $|bm_b\rangle$ and $\langle\beta m_\beta|$ either, since m_b and m_β are being summed over. All we have to rotate is $\langle am_a|$, $|\alpha m_\alpha\rangle$, and μ. When they are rotated, we get certain linear combinations of other components. Those are just the same linear combinations as when we rotate $\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle$, q.e.d.

We shall consider $((a\alpha^+|h|b\beta^+))$ as a matrix in "reduced line space." "Reduced space" is a function space which has only one state in it for every set of $(2j+1)$ magnetic substates of ordinary atomic function space. Thus, reduced space does not have any magnetic quantum numbers, but the other quantum numbers are the same as for ordinary space. Reduced space can be doubled, like ordinary space. If we know $\mathcal{H}$, the matrix h can be computed by multiplying both sides of (83) by $\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle$ and summing over m_a, m_α, and μ. According to (82), we get

$$((a\alpha^+|h|b\beta^+))=\sum_{\mu m_a m_b m_\alpha m_\beta}\langle j_\alpha m_\alpha|\mu^*|j_a m_a\rangle\times\langle\langle am_a\alpha^+m_\alpha{}^+|\mathcal{H}|bm_b\beta^+m_\beta{}^+\rangle\rangle\langle j_b m_b|\mu|j_\beta m_\beta\rangle. \quad (84)$$

If now we consider any function of $\mathcal{H}$, $f(\mathcal{H})$, it is also true that we can write

$$\sum_{m_b m_\beta}\langle\langle am_a\alpha^+m_\alpha{}^+|f(\mathcal{H})|bm_b\beta^+m_\beta{}^+\rangle\rangle\langle j_b m_b|\mu|j_\beta m_\beta\rangle=\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle((a\alpha^+|f(h)|b\beta^+)). \quad (85)$$

This can be proved by expanding $f(\mathcal{H})$ in a power series. Consider, for instance, the function $\mathcal{H}^2$. We have

$$\sum_{m_b m_\beta}\langle\langle am_a\alpha^+m_\alpha{}^+|\mathcal{H}^2|bm_b\beta^+m_\beta{}^+\rangle\rangle\langle j_b m_b|\mu|j_\beta m_\beta\rangle=\sum_{m_b m_\beta c m_c\gamma m_\gamma}\langle\langle am_a\alpha^+m_\alpha{}^+|\mathcal{H}|cm_c\gamma^+m_\gamma{}^+\rangle\rangle\times\langle\langle cm_c\gamma^+m_\gamma{}^+|\mathcal{H}|bm_b\beta^+m_\beta{}^+\rangle\rangle\langle j_b m_b|\mu|j_\beta m_\beta\rangle.$$

By Eq. (83), this can be written

$$\sum_{cm_c\gamma m_\gamma}\langle\langle am_a\alpha^+m_\alpha{}^+|\mathcal{H}|cm_c\gamma^+m_\gamma{}^+\rangle\rangle\times\langle j_c m_c|\mu|j_\gamma m_\gamma\rangle((c\gamma^+|h|b\beta^+)).$$

By a new application of (83), this is equal to

$$\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle\textstyle\sum_{c\gamma}((a\alpha^+|h|c\gamma^+))((c\gamma^+|h|b\beta^+))=\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle((a\alpha^+|h^2|b\beta^+)),$$

q.e.d.

The expression that we need to calculate in order to obtain the line shape is the right-hand side of (62). According to (56), (76), and (78), a matrix element of Δ can be written

$$\langle\langle am_a\alpha^+m_\alpha{}^+|\Delta|bm_b\beta^+m_\beta{}^+\rangle\rangle=\textstyle\sum_\mu\langle j_a m_a|\mu|j_\alpha m_\alpha\rangle\langle j_\beta m_\beta|\mu^*|j_b m_b\rangle\times((a\alpha^+|\delta|b\beta^+)), \quad (86)$$

with the definition

$$((a\alpha^+|\delta|b\beta^+))=(a|d|\alpha)(\beta|d^*|b). \quad (87)$$

Since $\mathcal{H}$, H_{0i}, $H_{0f}{}^+$ are all spherically symmetric, we can apply the considerations of the last three paragraphs when performing the sum over magnetic quantum numbers in the trace in (62). Since an equation similar to (84) holds for any function of any spherically symmetric operator, the result is the following equation for the line shape:

$$\pi\rho^{-1}F(\omega)=-\mathcal{I}\,\mathrm{Tr}[\delta(\omega-h_{0i}+h_{0f}{}^+-h)^{-1}], \quad (88)$$

where all operators are now in reduced line space. h is given by (84), δ is defined by (87), and h_{0i} and $h_{0f}{}^+$ are operators whose eigenvalues for a reduced state are the same as those of H_{0i} and $H_{0f}{}^+$ for the $(2j+1)$ states from which the reduced state was derived. To obtain

the line shape, we must now treat Eq. (88) in the same way we treated (62). But (88) represents an enormous simplification over (62) since we now have only one state where we used to have $(2j+1)$, and the order of all matrices that enter into the calculation is correspondingly reduced.

The matrix h defined by (84) vanishes whenever the angular momenta j_a and j_α differ by more than one unit, whenever j_b and j_β differ by more than one unit, and whenever the product of the parities of a and α differs from that of b and β. The matrix δ defined by (87) may be taken to vanish under exactly the same circumstances and, in addition, it vanishes unless the parities of a and α differ and those of b and β differ too. As a consequence, the only doubled reduced states that need to be considered in the calculation of (88) are those for which the angular momentum of the final state does not differ by more than one unit from the angular momentum of the initial state, and for which the two parities are different. In other words, we only need to consider doubled states that correspond to actually observed lines in the spectrum of the atom. Thus, the work of Sec. 6 is further simplified.

The "reduction to collision axes" is possible also here, as in the one-state case. When we calculate $\mathfrak{K}$ by (61), it is not necessary to average over all possible orientations of the collision. It is sufficient to compute $\mathfrak{K}$ with a convenient set of "collision axes." The summation in (84) does the averaging over all directions for us. This is because $((a\alpha^+|h|b\beta^+))$ is independent of any magnetic quantum number, and hence it will be the same for any orientation of the collision. It is easy to see, with the help of (80) and (81), that the two-state case of (61) and (84) reduces to the one-state case of (28) and (73) whenever one of the two components of a line is unaffected by the collisions.

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Photodetachment Cross Section and the Electron Affinity of Atomic Oxygen*

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Experiments and theory on the continuous absorption of radiation by atomic-oxygen negative ions are described and discussed. The absorption cross section for photon energies not too near threshold is obtained directly from one of the experiments. Theory and experiment are combined to give the cross section in the vicinity of threshold and a precise value of the electron affinity of atomic oxygen. The latter result is EA(O) $=1.465\pm0.005$ ev. The data are used for computation of the radiative attachment coefficient, and other applications of the experimental results are discussed.

INTRODUCTION

THE absorption of continuous radiation by the O^- ion leads to the photodetachment of the extra electron.[1,2] This process is partially responsible for the release of electrons and the destruction of negative ions in the sunlit ionosphere,[3] and provides a source of opacity in certain spectral ranges for high-temperature plasmas containing oxygen.[4] The potential astrophysical importance of O^- absorption is suggested by the influence of H^- photodetachment on the solar continuous spectrum.[5] Comparison of the experimental photodetachment cross section with values calculated using approximate atomic wave functions and potentials may be helpful in the theoretical study of related processes less susceptible to experiment, for example, elastic scattering of electrons by atomic oxygen.[6] From the photodetachment cross section one can compute the radiative attachment cross section by the principle of detailed balancing. Radiative attachment provides the limiting rate for ion formation at low pressures.

The photon energy E_0 at the threshold for continuous absorption from the lowest state of O^- to the lowest state of O is equal to the binding energy of the ion and hence to the physical electron affinity of the oxygen atom. Observation of this threshold then provides a direct method for determining the oxygen affinity, EA(O). An accurate value for this affinity is needed both for the interpretation of physical processes involving O^- and for determination of other thermochemical constants numerically related to the oxygen electron affinity.

Previous determinations of EA(O) from the photo-

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