THE THEORY OF DISPERSION PROFILES
IN ATTENUATION

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THE THEORY OF DISPERSION PROFILES IN ATTENUATION

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Abstract

This paper examines attenuation processes from the viewpoint of collision theory, using the optical theorem to connect attenuation cross-section σ and refractivity n with diagonal elements of the T matrix. This approach provides resonance profiles (for "natural" lines shapes) of the form

$$\sigma(\omega) = C + \frac{(\Gamma/2)B + (\omega-\omega_0)A}{(\omega-\omega_0)^2 + (\Gamma/2)^2}$$

$$n(\omega) - 1 = \frac{Nc}{2\omega}\left[\frac{(\Gamma/2)A - (\omega-\omega_0)B}{(\omega-\omega_0)^2 + (\Gamma/2)^2} - D\right]$$

where the profile parameters A, B, C, D, Γ, ω_0 are given in terms of atomic matrix elements.

Part I reviews the notion of resonances. Part II summarizes the relevant results of collision theory, stressing physical interpretation, and gives a definition for excited (or resonance) states based on a simple partition of basis states into two classes. Part III applies perturbation theory to the calculation of resonance profiles. Part IV applies these results specifically to the attenuation and refraction of photons by tenuous gases, with particular attention paid to the profiles of autoionizing lines.

I. SPECTRAL LINES AS RESONANCES

A. The Nature of Resonance Observations

Rate coefficients or cross-sections for collision processes, measured as a function of incident projectile energy E, often show abrupt variations (<u>resonances</u>) as the energy passes some value E_0. Typically, this energy dependence or <u>profile</u> follows the dispersion formula

$$Q(E) = C(E) + \frac{(\Gamma/2)B + (E-E_0)A}{(E-E_0)^2 + (\Gamma/2)^2}, \tag{1.1}$$

where the background C(E) varies only slowly with energy, and B, A, E_0 (the resonance energy) and Γ (the resonance width) are parameters independent of E. (Appendix A discusses several alternative parameterization of Q(E)). Actual observations are, of course, influenced by effects of finite sample temperature, density and thickness -- effects that are treated in the discipline of radiative transfer[1] and are here ignored: the present paper concerns only the "natural" shape of absorption lines.

For inelastic collision processes, parameter A usually vanishes, and the formula[2]

$$Q(E) = C(E) + \frac{(\Gamma/2)B}{(E-E_0)^2 + (\Gamma/2)^2} \tag{1.2}$$

applies. In observations of absorption spectra, such resonances appear as dark absorption lines or spectral lines. Observations of the refractive index usually reveal a profile with $B = 0$:[4]

$$Q(E) = C(E) + \frac{(E-E_0)A}{(E-E_0)^2 + (\Gamma/2)^2} . \tag{1.3}$$

The explanation of such resonance phenomena in the absorption and refraction of light traces back[5] to the work of Sellmeier[6] and von Helmholtz[7] (Lord Rayleigh[8] pointed out that Maxwell anticipated these results in posing a Cambridge Tripos Exam in 1869). From a more modern viewpoint, attenuation occurs when an atom in state A absorbs a photon γ to produce the excited atomic state A*:

$$A + \gamma \rightarrow A^* .$$

The excited state subsequently decays by emitting one or more photons:

$$A^* \rightarrow A + \gamma .$$

Since few emitted photons reappear in the direction of the incident beam, the encounter depletes the photon beam, and an absorption line develops. (This simplified picture applies only when the absorbing medium is cool and optically thin.)

When the energy of A^* exceeds the first ionization limit, decay by electron emission (autoionization[9]) may also occur:

$$\begin{tikzcd} & A + \gamma \\ A^* \arrow[ur] \arrow[dr] & \\ & A^+ + e \end{tikzcd} .$$

In turn, decay by photon or electron emission may occur through several modes or decay channels[10] corresponding to the various possible states of the projectile and residual atom or ion.

Autoionizing states (also called compound states, resonance states, metastable states, collision complexes) can, of course, be formed either by electron bombardment of A^+ or by photoexcitation of A:

$$\begin{tikzcd} A^+ + e \arrow[dr] & & A^+ + e \\ & A^* \arrow[ur] \arrow[dr] & \\ A + \gamma \arrow[ur] & & A + \gamma \end{tikzcd} .$$

Not all projectile encounters lead to formation of such compound states: direct processes, such as photoionization and Thomson scattering of photons, and Coulomb scattering or potential scattering of electrons, may compete with compound-state formation. These excited states, therefore, influence such processes as[12] elastic and inelastic scattering of electrons, electron capture (dielectronic recombination[13]), and photon attenuation. Each type of observation discloses slightly different aspects of the compound state. In Eq. (1.1), the parameters C(E), B, and A for a particular resonance vary with the type of projectile, scattering angle, and type of reaction product observed. The resonance energy E_0 and resonance width Γ depend primarily on the properties of the compound state, not on the mode of formation or decay. Although I have explicitly described the interaction of a photon projectile with an atomic target, the conclusions apply to other projectiles colliding with either atoms or nuclei. To illustrate how A, B, and C(E) may vary while E_0 and Γ remain fixed, Fig. 1[14] shows cross-sections for several processes that can form compound states of the nucleus Si^{28}. One must similarly anticipate that observations of electron-scattering cross-sections will not completely determine photon-attenuation cross-sections.

B. Theories of Resonance Phenomena

The conventional quantum theory of atomic absorption-line profiles[15] presumes that the decay of a compound state is not coherent with the formation process. One may then consider the decay of a system from a prepared initial state, the compound state. This leads to a Lorentz profile, Eq. (1.2), with a width equal to $\hbar$ times the decay rate of the compound state.

Such an approach is reasonable for ordinary radiative decay, which proceeds quite slowly on an atomic time scale (e.g., an electron circles the first Bohr orbit of hydrogen in 1.5×10^{-16} sec; the mean life of the 2p level of hydrogen is 1.6×10^{-9} sec). However, autoionization proceeds on a much faster time scale (typically 10^{-14} sec) than radiative decay, and it is no longer evident that formation and decay may be treated separately. Although it is possible to predict the position and width of resonance lines by considering the decay of prepared states[18], a full description of asymmetric profiles requires examination of the preparation process.

The quantum theory of scattering[19] provides a more satisfactory foundation for a description of absorption-line profiles. Such an approach ignores unobserved processes, such as the preparation of an unstable state at some precise time, and deals directly with scattering amplitudes and cross-sections. Energy, rather than time, is sharply defined.

A number of authors have now developed general formalisms for describing reactions and resonance processes within the framework of quantum scattering theory[24-32]. Although these authors initially directed their attention to nuclear reactions, many of their results apply equally to atomic collision processes. Subsequently other workers have applied and extended these techniques to the study of electron scattering by atoms[33-38] and to the prediction of resonance energies[39,40]. For summaries of electron-resonance observations, the reader should consult the recent comprehensive reviews by Burke[12] and by Smith[41].

Despite this active study of electron scattering, the peculiarities of photon-induced processes -- autoionization in particular -- have not been explicitly examined from the viewpoint of reaction theory. Current investigations of autoionization all follow the approach of Fano and his associates[42-45], who diagonalize the Hamiltonian by mixing discrete and continuum states. It is instructive to see how their results emerge from collision theory[46].

Furthermore, the details of resonance <u>attenuation</u> (as distinguished from scattering or specific reaction processes) have not been fully examined from the viewpoint of the "unified reaction theory."[25] In the present article I wish to point out how this formalism, by providing an explicit connection between profile parameters and atomic matrix elements, aids the interpretation of attenuation profiles.

Although nuclear and atomic collision processes may be viewed as two aspects of a general physics of collisions, they differ in one important respect. During a nuclear collision, the target nucleus remains isolated from any disturbance apart from the projectile. Atomic collisions, on the other hand, occur while the target atom is subjected to a variety of disturbances from surrounding atoms. In practice, such disturbances can significantly distort the "natural" attenuation profiles of isolated atoms and any realistic theory of line shapes must account for the influence of the surrounding medium[47]. However, the present paper will concentrate on collisions with isolated target atoms. The results therefore apply to attenuation by tenuous gases.

II. SUMMARY OF COLLISION THEORY

A. The Scattering Matrix

Scattering theory provides a useful means of visualizing the atomic processes that are responsible for absorption lines. One imagines a wave-packet of known properties impinging on a stationary scattering center.[18-23] One then examines the waves that emerge, under the action of the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \underset{\sim}{\Psi}(t) = H \underset{\sim}{\Psi}(t) \quad . \tag{2.1}$$

To describe the evolution of $\underset{\sim}{\Psi}(t)$, one may introduce some convenient set of basis states. These many-particle states, degenerate eigenstates of an operator H^o,

$$(H^o - E_a)\psi_a = 0 \, , \qquad \int_a |\psi_a\rangle\langle\psi_a| = 1 \quad , \qquad \langle\psi_a|\psi_b\rangle = \delta_{ab} \, , \tag{2.2}$$

are labelled by a set of quantities <u>a</u> (both discrete and continuous) that can completely describe the status of the projectile and the target particles.[48]

The choice of basis states defines the perturbing interaction V, the difference between the actual Hamiltonian H and the operator H^o

$$H = H^{o} + V \;. \tag{2.3}$$

(Conversely, a choice of V fixes the basis states.) As defined here, V is entirely responsible for transitions from one basis state to another during the course of a scattering event.

A typical scattering event begins in the remote past ($t \to -\infty$) with a wave-packet projectile moving toward the target from a great distance. The interaction V is assumed to vanish when the projectile is far from the atom, so that this initial situation may be described as a superposition of basis states representing a definite target state and a wave-packet projectile:

$$\underset{\sim}{\Psi}(t \to -\infty) = \int_{\alpha} A_{\alpha}\, e^{-iE_{\alpha}t/\hbar}\, \psi_{\alpha} = e^{-iH^{o}t/\hbar} \int_{\alpha} A_{\alpha}\psi_{\alpha} \;. \tag{2.4}$$

As time progresses, the wave-packet moves into the scattering region and the interaction V alters both the wave-packet and the target atom. The modified state may be written as[20]

$$\underset{\sim}{\Psi}(t) = \int_{\alpha} A_{\alpha}\, e^{-iE_{\alpha}t/\hbar}\; U(t,-\infty)\,\psi_{\alpha} \;, \tag{2.5}$$

where the time-development operator $U(t,t_{o})$ determines the change in $\underset{\sim}{\Psi}(t)$ caused by the interaction V. It satisfies the integral equation,[20]

$$U(t,t_0) = 1 - i \int_{t_0}^{t} dt' \, e^{iH^0 t'/\hbar} \, V \, e^{-iH^0 t'/\hbar} \, U(t', t_0) \quad . \tag{2.6}$$

Ultimately, as t → ∞, the wave-packet passes out of the scattering region. Again the solution $\underset{\sim}{\Psi}(t)$ becomes expressible as a superposition of unperturbed eigenstates of H^0:

$$\underset{\sim}{\Psi}(t \to \infty) = \sum\!\!\!\!\!\!\int_b \psi_b \, e^{-iE_b t/\hbar} \sum\!\!\!\!\!\!\int_a S_{ba} A_a \quad . \tag{2.7}$$

The element S_{ba} of the scattering, or $\underset{\sim}{S}$-matrix[49] gives the component ψ_b of the final state $\underset{\sim}{\Psi}(t \to \infty)$ that emerges from the initial component ψ_a:

$$S_{ba} = \langle \psi_b | U(\infty, -\infty) | \psi_a \rangle \, . \tag{2.8}$$

Although the initial and final states ψ_a and ψ_b must be states for which the system has a projectile at infinite separation (so-called open channels or continuum states), during the collision process other states (referred to as closed channels or discrete bound states) will become temporarily excited. These temporary excitations are responsible for resonance processes. The mathematical structure of $U(t,t_o)$ contains a description of all such processes, although this is not obvious from Eq. (2.6).

B. The Lippmann-Schwinger Equation

As energy measurements sharpen, one ultimately replaces the wave-packet projectile with monochromatic wave trains; at a large distance from the target these trains consist of incoming plane waves and outgoing spherical waves. These wave trains have the form, at all times.

$$\underset{\sim}{\Psi}(t) = \int_a A_a e^{-iE_a t/\hbar} \Psi_a^+ = e^{-iHt/\hbar} \int_a A_a \Psi_a^+ , \tag{2.9}$$

where Ψ_a^+ is an eigenstate of the total Hamiltonian:[50]

$$(H^0 + V - E_a)\Psi_a^+ = 0 . \tag{2.10}$$

Equation (2.10) and the boundary condition, that scattered waves should ultimately move spherically <u>outward</u> from the target, are commonly combined into the Lippmann-Schwinger equation:[20]

$$\Psi_a^+ = \psi_a + \lim_{\eta \to 0^+} \left[\frac{1}{E_a + i\eta - H^0} V \Psi_a^+ \right] . \tag{2.11}$$

This symbolic operator equation stands for an integral equation, in which $\eta \to 0^+$ after integration. From an operational standpoint, such an integral means,[51] for an arbitrary function $F(E)$,

$$\lim_{\eta \to 0^+} \int_b \frac{F(E_b)}{E_a \pm i\eta - E_b} = \int_b' \frac{F(E_b)}{E_a - E_b} \mp i\pi \int_b \delta(E_a - E_b) F(E_a) , \tag{2.12}$$

where $\mathop{S}'_{b}$ denotes a sum over states excluding these with $E_b = E_a$ (the Cauchy principle-part of the integral over dE_b). Thus the requirement for outgoing scattered waves leads to the equation:[52]

$$\Psi_a^+ = \psi_a + \int'_b \frac{\psi_b \langle\psi_b|V|\Psi_a^+\rangle}{E_a - E_b} - i\pi \int_b \delta(E_a - E_b)\, \psi_b \langle\psi_b|V|\Psi_a^+\rangle . \tag{2.13}$$

These eigenstates of H preserve the orthonormality of ψ_a and ψ_b:[53]

$$\langle\Psi_a^+|\Psi_b^+\rangle = \delta_{ab} . \tag{2.14}$$

However, unlike the eigenstates of H^o, these "perturbed" scattering states do not form a complete set, since they do not include closed channels (i.e., bound states).[26] The wave function for a bound state is concentrated near the target and so cannot be observed at large projectile separation.

Equation (2.13) provides an integral equation for the scattering state Ψ_a^+. It is more convenient to transform that equation, using the definitions[54]

$$G(E) \equiv \frac{1}{E^+ - H^o - V} , \qquad G^o(E) \equiv \frac{1}{E^+ - H^o} , \qquad E^+ \equiv E + i\eta , \tag{2.15}$$

and the identity

$$G(E) = \frac{1}{E^+ - H^o} + \frac{1}{E^+ - H^o} V \frac{1}{E^+ - H^o - V} \equiv G^o + G^o V G , \tag{2.16}$$

into the operator equation

$$\Psi_a^+ = \psi_a + G(E_a)\,V\,\psi_a \;. \tag{2.17}$$

This formula places the disturbing influence of the interaction V into the operator G(E) rather than into the wavefunction Ψ_a^+.

As a third alternative, one can introduce the reaction operator $\mathcal{T}(E)$,[55]

$$\mathcal{T}(E) \equiv V + VG(E)V \tag{2.18}$$

and then write Eq. (2.17) as

$$\Psi_a^+ = \psi_a + G^0(E)\,\mathcal{T}(E)\psi_a \;. \tag{2.19}$$

$\mathcal{T}(E)$ has the matrix elements

$$T_{ba} \equiv \langle\psi_b|\mathcal{T}|\psi_a\rangle = \langle\psi_b|V|\Psi_a^+\rangle \;. \tag{2.20}$$

The scattering description is now contained in the structure of the reaction operator $\mathcal{T}(E)$, a non-Hermitian many-particle "effective interaction."

The connection between the $\underset{\sim}{S}$-matrix, and the quantities Ψ_a^+ or G(E) or $\mathcal{T}(E)$, becomes apparent when Eq. (2.9) is rewritten in terms of basis states:

$$\underset{\sim}{\Psi}(t) = \int_a A_a\, e^{-iE_a t/\hbar} \int_b \psi_b \langle \psi_b | \Psi_a^+ \rangle. \tag{2.21}$$

In the limit t → ∞ this becomes[20]

$$\underset{\sim}{\Psi}(t \to \infty) = \int_a A_a\, e^{-iE_a t/\hbar} \left\{ \psi_a - 2\pi i \int_b \delta(E_b - E_a)\, \psi_b\, T_{ba} \right\}. \tag{2.22}$$

The scattering matrix of Eq. (2.8) can thus be recognized as[20]

$$(\underset{\sim}{S} - 1)_{ba} = -2\pi i\, \delta(E_a - E_b)\, T_{ba}. \tag{2.23}$$

The delta function $\delta(E_a - E_b)$ insures energy conservation in the collision; only matrix elements of $\underset{\sim}{S}$ between states of equal energy are required.[56]

C. Observable Quantities

The physical content of the $\underset{\sim}{S}$-matrix is best displayed by rewriting Eq. (2.9) as

$$\underset{\sim}{\Psi}(t \to \infty) = e^{-iH^0 t/\hbar} \int_a A_a \left\{ \psi_a \left[1 + (\underset{\sim}{S} - 1)_{aa}\right] + \int_{b \neq a} \psi_b\, S_{ba} \right\}. \tag{2.24}$$

One can then see that the incident component ψ_a gives rise to a transmitted wave,

$$\psi_a^{trans} \equiv \psi_a \left[1 + (\underset{\sim}{S} - 1)_{aa} \right] \tag{2.25}$$

and scattered waves

$$\psi_a^{scatt} \equiv \underset{b \neq a}{\mathrm{S}} \psi_b S_{ba} = \underset{b \neq a}{\mathrm{S}} \psi_b (\underset{\sim}{S} - 1)_{ba} \tag{2.26}$$

The transmitted wave ψ_a^{trans} is altered in phase and diminished in amplitude compared with ψ_a. Components of the scattered wave ψ_a^{scatt} differ from ψ_a in propagation direction or in angular momentum or in other quantum-number labels. The requirement that $\underset{\sim}{S}$ be a unitary matrix,[20]

$$\underset{\sim}{S}^{\dagger} \underset{\sim}{S} = \underset{\sim}{S} \underset{\sim}{S}^{\dagger} = 1 \quad \text{or} \quad \underset{b}{\mathrm{S}} (\underset{\sim}{S}^{\dagger})_{ab} S_{bc} = \delta_{bc} , \tag{2.27}$$

expresses the fact that, if flux is to be conserved, scatterings into state ψ_b must deplete the initial state ψ_a.

With the aid of the formula[51]

$$\delta(E_a - E_b) = -\frac{i}{\hbar} \int dt \quad \exp\left[i (E_b - E_a) t / \hbar \right] \tag{2.28}$$

one can write the probability for a transition a → b ≠ a during the collision interval (t → - ∞ to t → ∞) as[20]

$$\begin{aligned} |(\underset{\sim}{S}-1)_{ba}|^2 &= \frac{2\pi}{\hbar}\,\delta(E_b-E_a)\,|T_{ba}|^2 \int_{-\infty}^{\infty} dt \\ &\equiv w_{a\to b} \int dt \end{aligned} \qquad (2.29)$$

This probability increases at the constant rate $w_{a \to b}$. If F_a denotes the flux of incident projectiles in state ψ_a, then the cross section for the process $a \to b \neq a$, defined as[57]

$$\sigma(a\to b) \equiv \frac{\text{rate of } a\to b \text{ per target}}{\text{flux of projectiles}} = \frac{w_{a\to b}}{F_a} \qquad (2.30)$$

can be written, as is well known,[20-23,58]

$$\sigma(a\to b) = \frac{2\pi}{\hbar F_a}\,\delta(E_b-E_a)\,|T_{ba}|^2 . \qquad (2.31)$$

For example, if the labels a and b include the direction of projectile motion, $\sigma(a \to b)$ gives the angular distribution of the scattering process.

Macroscopic descriptions[59-60] of wave propagation commonly employ an index of refraction (or a dielectric constant) to express the influence of the propagation medium on the incident wave. A plane wave propagating along the z-axis through vacuum has the form

$$\psi(z,t) = \psi(0,0)\exp[i(kz-\omega t)] = \psi(0,t)\,e^{ikz} . \qquad (2.32)$$

When passing through a uniform medium, the propagation vector k alters to $\tilde{\underset{\sim}{n}}k$, where $\tilde{\underset{\sim}{n}}$ is the (complex) index of refraction. A thin slab of matter, of thickness dz, changes the incident plane wave $\psi(z,t)$ to a transmitted wave plus a scattered wave:

$$\psi(z,t) \longrightarrow \psi^{\text{trans}}(z,t) + \psi^{\text{scatt}}(z,t) \tag{2.33}$$

where

$$\psi^{\text{trans}}(z,t) = \psi(0,t)\ \exp\left[i k(z-dz) + i\tilde{\underset{\sim}{n}} k\, dz\right] . \tag{2.34}$$

The intensity of this transmitted wave diminishes exponentially with a decay constant (or absorption coefficient) defined as $N\sigma$, where N is the density of absorbers and σ is the attenuation cross section:

$$\begin{aligned} |\psi^{\text{trans}}(z+dz,t)|^2 &= |\psi(z,t)|^2 \exp(-2k\,dz\ \mathrm{Im}\,\tilde{\underset{\sim}{n}}) \\ &\equiv |\psi(z,t)|^2 \exp(-N\sigma\,dz) . \end{aligned} \tag{2.35}$$

Therefore $(\tilde{\underset{\sim}{n}} - 1)$ may be written:

$$\tilde{\underset{\sim}{n}} - 1 = (n-1) + i\left(\frac{N\sigma}{2k}\right) . \tag{2.36}$$

The real part, (n - 1), is the refractivity,[59] the complex part, ($N\sigma/2k$), is proportional to the absorption coefficient. For a thin slab, the exponential may be expanded as a power series in dz, giving

$$\psi^{\mathrm{trans}}(z,t) \cong \psi(z,t)\left[1 + ik\,(\underset{\sim}{\tilde{n}} - 1)\,dz\right] . \qquad (2.37)$$

To connect this description with the $\underset{\sim}{S}$-matrix, one may again use formula (2.28) and write Eq. (2.25) as

$$\psi^{\mathrm{trans}}_{a} = \psi_a \left[1 - \frac{i}{\hbar}\, T_{aa} \int dt \right] . \qquad (2.38)$$

Here, as in Eq. (2.29), $\psi^{\mathrm{trans}}_{a}$ changes at a steady rate over the infinite interval $\int dt$. The infinitesimal change of a flux F_a (projectiles per cm^2 per sec) passing through a medium of density N_a (targets per cm^3) may then be written

$$\left[1 - \frac{i}{\hbar}\, T_{aa}\, \frac{N_a}{F_a}\, dz \right] = \left[1 + ik_a\,(\underset{\sim}{\tilde{n}}_a - 1)\,dz\right] . \qquad (2.39)$$

Thus the index of refraction may be identified as[61]

$$\underset{\sim}{\tilde{n}}_a - 1 = -\frac{N_a T_{aa}}{\hbar k_a F_a} . \qquad (2.40)$$

The subscript a denotes the projectile state (e.g., energy and polarization) as well as the target state.

Equation (2.42) gives the refractivity

$$n_a - 1 = -\frac{N_a}{\hbar k_a F_a} \mathcal{R}e\,(T_{aa}) \tag{2.41}$$

and the attenuation cross section

$$\sigma(a) = -\frac{2}{\hbar F_a} \mathcal{I}m\,(T_{aa}). \tag{2.42}$$

The conventional proof[20] of Eq. (2.42), often referred to as the <u>optical theorem</u> of Bohr, Peierls, and Placzek,[62] relies on the fact that attenuation is the sum of all the processes that remove a projectile from state ψ_a. The attenuation cross-section is therefore the sum of all possible scattering and reaction cross-sections,

$$\begin{aligned} \sigma(a) &= \mathop{\mathrm{S}}_{b \neq a} \sigma(a \rightarrow b) \\ &= \frac{2\pi}{\hbar F_a} \mathop{\mathrm{S}}_{b \neq a} \delta(E_b - E_a)\, |T_{ba}|^2 . \end{aligned} \tag{2.43}$$

Equation (2.42) then obtains when one employs the unitary relation, Eq. (2.27).

From Eq. (2.40) it follows that, when T_{aa} has the frequency dependence

$$\frac{T_{aa}}{\hbar k_a F_a} = \frac{B - iA}{\omega - \omega_0 + i(\Gamma/2)} , \tag{2.44}$$

the abosrption coefficient is obtained from

$$\mathcal{I}m\,(\underset{\sim}{\tilde{n}}) = N_a \left[\frac{(\Gamma/2)\,B + (\omega-\omega_0)\,A}{(\omega-\omega_0)^2 + (\Gamma/2)^2} \right] \tag{2.45}$$

and the refractivity is

$$\mathcal{R}e\,(\underset{\sim}{\tilde{n}} - 1) = N_a \left[\frac{(\Gamma/2)\,A - (\omega-\omega_0)\,B}{(\omega-\omega_0)^2 + (\Gamma/2)^2} \right] . \tag{2.46}$$

These formulas provide a connection between attenuation measurements and refracitivity measurements,[63] particularly useful for autoionizing lines (for which A is generally not zero). They are, of course, simply special cases of the Kramers-Kronig dispersion relations[64] obtained from the real and imaginary parts of the equation:

$$\underset{\sim}{\tilde{n}}(\omega) - 1 = \frac{i}{\pi}\,\mathcal{P}\int_{-\infty}^{\infty} \frac{[\,\underset{\sim}{\tilde{n}}(\omega) - 1\,]}{\omega - \omega'}\,d\omega' . \tag{2.47}$$

When $|\underset{\sim}{\tilde{n}}|$ is close to unity, the dielectric constant ϵ_a and polarizability α_a may be obtained from[65]

$$\epsilon_a - 1 = 4\pi N_a \alpha_a = |\underset{\sim}{\tilde{n}}_a|^2 - 1 \cong 2\,(\underset{\sim}{\tilde{n}}_a - 1) . \tag{2.48}$$

That is,

$$\epsilon_a - 1 = -\frac{2 N_a T_{aa}}{\hbar k_a F_a} , \qquad \alpha_a = -\frac{T_{aa}}{2\pi\hbar k_a F_a} . \tag{2.49}$$

In practice, one usually observes a cross section or refractivity averaged over some degenerate set of initial states, say $\mathfrak{A}$, which may include projectile polarization and various angular-momentum quantum numbers of the target. The relevant quantities are then

$$\bar{\sigma}(\mathfrak{A}) = \frac{1}{\varpi} \sum_{a\in\mathfrak{A}} \sigma(a) = -\frac{2}{\hbar F_a \varpi} \sum_{a\in\mathfrak{A}} \mathcal{I}m\,(T_{aa}) \tag{2.50}$$

$$\bar{n}(\mathfrak{A}) - 1 = -\frac{1}{\hbar k_a F_a \varpi} \sum_{a\in\mathfrak{A}} \frac{N_a}{N} \mathcal{R}e\,(T_{aa}) \tag{2.51}$$

where the statistical weight is the number of states included in the set :

$$\varpi = \sum_{a\in\mathfrak{A}} 1 \tag{2.52}$$

and N is the total number of targets

$$N = \sum_{a\in\mathfrak{A}} N_a . \tag{2.53}$$

Hitherto, attenuation profiles have usually been determined from Eq. (2.43). Often a particular process dominates the scattering, and an accurate attenuation cross-section obtains from only one or two terms in the summation. The present paper points out the usefulness of Eq. (2.42) as a starting point for calculations.

D. Resonances

In principle, the $\underset{\sim}{S}$-matrix (or Ψ^+ or G) contain a complete description of all possible collision processes, but practical difficulties often intervene when one attempts to extract the information.

As Siegert[66] pointed out, the analytic properties of the scattering matrix lead to cross-section profiles of the form of Eq. (1.1). More recently, the *Mittag-Leffler expansion*[67] of a function in rational fractions,

$$F(z) = F(0) + \sum_n b_n \left[\frac{1}{z - a_n} + \frac{1}{a_n} \right] \tag{2.54}$$

has been used as the basis for an elaborate parameterization of $\underset{\sim}{S}(E)$ by Humblet and Rosenfeld.[28] While such an approach has proven fruitful in formal investigations[68] it does not by itself provide a complete prescription for computing the relevant parameters.

A second avenue of approach makes use of appropriate joining conditions for wave functions at the boundary of the interaction region.[69-71] Here too, the formalism has provided a useful parameterization of nuclear reactions.

In atomic processes, where the nature of the interaction between particles is well known, it has proven more useful to relate scattering amplitudes with matrix elements. To describe resonance processes, it is only necessary to partition the basis states into two classes. This partitioning is most easily carried out with the aid of projection operators[72] defined by

$$1 = P + Q , \qquad P^2 = P , \qquad Q^2 = Q , \qquad PQ = QP = 0 . \tag{2.55}$$

Quite simply, $Q\Psi$ is the component of the state Ψ contained in some selected subspace (to be referred to as <u>closed channels</u>, resonance states, or bound states), and $P\Psi$ is the remainder (to be called <u>open channels</u> or continuum states). The essential point is that the initial state is contained entirely in $P\Psi$; $Q\Psi$ contains no component of this state. A precise specification of $Q\Psi$ will be discussed below. If we now follow Messiah[74] and write the Hamiltonian as

$$H = (PHP + QHQ) + (PHQ + QHP) \equiv H^1 + H^2 \tag{2.56}$$

and use the identity

$$G = \frac{1}{E^+ - H^1 - H^2} = \frac{1}{E^+ - H^1} + \frac{1}{E^+ - H^1} H^2 \frac{1}{E^+ - H^1 - H^2}$$

$$= \frac{1}{E^+ - H^1} + \frac{1}{E^+ - H^1 - H^2} H^2 \frac{1}{E^+ - H^1} \, . \qquad (2.57)$$

It is easy to verify that[75]

$$PGP = \mathcal{G}_P (PHQ)(QGQ) \qquad (2.58a)$$

$$QGP = (QGQ)(QHP)\mathcal{G}_P \qquad (2.58b)$$

$$PGQ = \mathcal{G}_P + \mathcal{G}_P (PHQ)(QGQ)(QHP)\mathcal{G}_P \qquad (2.58c)$$

where[76]

$$\mathcal{G}_P = P \frac{1}{E^+ - PHP} P \, . \qquad (2.59)$$

Equations (2.58) express the operator G in terms of the more restricted operators $\mathcal{G}_P$ and QGQ. In turn, QGQ may be found by substituting the above expression for PGQ into

$$Q(E - H)GQ = Q \qquad (2.60)$$

to obtain

$$\left[E - QHQ - (QHP)\mathcal{G}_P(PHQ)\right]QGQ \quad = Q\,. \tag{2.61}$$

It follows that

$$QGQ \quad = \quad Q\left[E - QHQ - (QHP)\mathcal{G}_P(PHQ)\right]^{-1}Q\,. \tag{2.62}$$

If now we write $H = H^o + V$, and require that basis states be eigenstates of H^o,

$$PH^oQ = QH^oP = 0\ , \tag{2.63}$$

then we can write the $\mathcal{J}$ operator (Eq. (2.18)) as

$$\begin{aligned}\mathcal{J} &= V + V(PGP + PGQ + QGP + QGQ)V \\ &= V + V\mathcal{G}_PV \\ &\qquad + (V + V\mathcal{G}_PV)Q\left[E - QHQ - QV\mathcal{G}_PVQ\right]^{-1}Q(V + V\mathcal{G}_PV)\,.\end{aligned} \tag{2.64}$$

This equation can be written more succinctly by introducing the operator[76]

$$\mathfrak{t} \equiv \mathfrak{t}(P,E) = V + V\mathcal{G}_PV\ . \tag{2.65}$$

The reaction operator is then written:[77]

$$\mathcal{J} = \mathcal{t} + \mathcal{t}\, Q \frac{1}{E - H^{\circ} - Q\mathcal{t}Q} Q\, \mathcal{t} . \tag{2.66}$$

This equation permits a useful physical interpretation of the reaction operator $\mathcal{J}$.[29] The first term, $\mathcal{t}$, gives scattering in the absence of a selected collection of states Q. Physically, this corresponds to direct reactions and potential scattering; $\mathcal{t}$ is a many-particle generalization of the optical potential.[73] The second term describes the influence of the states Q, and it gives rise to resonances.

To see this resonance structure most clearly, suppose Q projects only a <u>single</u> bound eigenstate of H^{o}, ψ_n, which is orthogonal to all remaining states;[40]

$$Q = |\psi_n\rangle\langle\psi_n| \tag{2.67a}$$

$$(H^{\circ} - e_n)\psi_n = 0 \tag{2.67b}$$

Then the elements of $\mathcal{J}$ are

$$T_{ba} = \langle\psi_b|\, \mathcal{t}(n,E)\, |\psi_a\rangle + \frac{\langle\psi_b|\, \mathcal{t}(n,E)\, |\psi_n\rangle\langle\psi_n|\, \mathcal{t}(n,E)\, |\psi_a\rangle}{E - e_n + \langle\psi_n|\, \mathcal{t}(n,E)\, |\psi_n\rangle} . \tag{2.68}$$

Since matrix elements of $\mathcal{t}$ are complex quantities, this expression can be written:

$$T_{ba} = D(n,E) - i\,C(n,E) + \frac{B(n,E) - i\,A(n,E)}{E - E_n(E) + i\,\Gamma_n(E)/2} \tag{2.69}$$

If the quantities A(n,E), B(n,E), C(n,E), D(n,E), and

$$E_n(E) = e_n + \mathcal{R}e \langle \psi_n | t | \psi_n \rangle , \tag{2.70a}$$

$$\Gamma_n(E) = -2\, \mathcal{I}m \langle \psi_n | t | \psi_n \rangle , \tag{2.70b}$$

vary only slowly with energy over an interval near $E = e_n$, then one can speak of a resonance at energy $E_n(e_n)$ with a width $\Gamma_n(e_n)$.

More generally, if Q projects out several (or all) closed channels, the $\mathcal{T}$ matrix has the form

$$T_{ba} = \langle \psi_b | t | \psi_a \rangle + \sum_{n,m} \langle \psi_b | P t Q | \psi_n \rangle \langle \psi_n | Q [E - H^0 - t]^{-1} Q | \psi_m \rangle \times \langle \psi_m | P t P | \psi_a \rangle . \tag{2.71}$$

The scattering resonances contained in the second term of Eq. (2.66) are basically "many-channel" resonances that exist because of the coupling between the incident channel and other channels. Such resonances include the familiar absorption lines of atoms. However, another type of broad resonance-like variation in scattering amplitudes can originate in the potential scattering term $\langle \psi_b | t | \psi_a \rangle$. Such single-channel "resonances" or size-resonances can occur at incident energies which permit an integral number of nodes for the projectile wave function within a complex potential-well.

Several methods might be used to evaluate Eq. (2.71). For example, one could obtain the matrix of $(E - H^0 - \mathscr{t})$ in some simple basis and then invert this matrix.[75] In the present paper, I shall evaluate Eq. (2.71) by obtaining[78] (approximately) states that satisfy the equation

$$\langle \Phi_N | Q(H^0 + \mathscr{t})Q | \Phi_K \rangle = [E_K - i(\Gamma_K/2)]\,\delta_{KN} \equiv \mathcal{E}_K \delta_{KN} . \tag{2.72}$$

Then T_{ba} becomes

$$T_{ba} = \langle \psi_b | P\mathscr{t}P | \psi_a \rangle + \sum_K \frac{\langle \psi_b | P\mathscr{t}Q | \Phi_K \rangle \langle \Phi_K | P\mathscr{t}Q | \psi_a \rangle}{E - E_K(E) + i\,(\Gamma_K(E)/2)} \tag{2.73}$$

where $E_K(E)$ and $\Gamma_K(E)$ are given by

$$E_K(E) = e_K + \mathrm{Re}\, \langle \Phi_K | Q\mathscr{t}Q | \Phi_K \rangle , \tag{2.74a}$$

$$\Gamma_K(E) = -2\, \mathrm{Im}\, \langle \Phi_K | Q\mathscr{t}Q | \Phi_K \rangle . \tag{2.74b}$$

If Q includes all bound states, then each of these contributes a resonance to T_{ba}. For simplicity, I shall employ a subscript notation for matrix elements of $\mathscr{t}$,

$$t_{ba} \equiv \langle \psi_b | \, P t P \, | \psi_a \rangle , \tag{2.75a}$$

$$t_{bK} \equiv \langle \psi_b | \, P t Q \, | \Phi_K \rangle , \tag{2.75b}$$

$$t_{KK} \equiv \langle \Phi_K | \, Q t Q \, | \Phi_K \rangle . \tag{2.75c}$$

Subscripts a and b refer to open channels, subscript K refers to a closed channel or resonance state. It also proves useful to write t_{bK} and t_{Ka} as the sum of two Hermitian parts:[79]

$$t_{bK} = t_{bK}^{(r)} + i\, t_{bK}^{(i)} = t_{Kb}^{(r)\,*} + i\, t_{Kb}^{(i)\,*} . \tag{2.76}$$

With this notation, Eq. (2.73) reads:

$$T_{ba} = t_{ba} + \sum_K \frac{(t_{bK}^{(r)} + i\, t_{bK}^{(i)})(t_{Ka}^{(r)} + i\, t_{Ka}^{(i)})}{E - e_K - t_{KK}} . \tag{2.77}$$

In particular, the diagonal elements are

$$T_{aa} = t_{aa} + \sum_K \frac{|t_{aK}^{(r)}|^2 - |t_{aK}^{(i)}|^2 + i\left[t_{aK}^{(r)} t_{Ka}^{(i)} + t_{aK}^{(i)} t_{Ka}^{(r)}\right]}{E - e_K - t_{KK}} . \tag{2.78}$$

Suppose now that we write this in the form

$$\frac{2\, T_{aa}}{\hbar F_a} = D - iC + \sum_K \frac{B_K - i A_K}{E - E_K + i(\Gamma_K/2)} , \tag{2.79}$$

by defining the following quantities (all dependent on $E \equiv E_a$):

$$A_k = -\frac{4}{\hbar F_a} \mathcal{R}e \left[t^{(r)}_{ak} \, t^{(i)}_{ka} \right] \tag{2.80}$$

$$B_k = \frac{2}{\hbar F_a} \left[|t^{(r)}_{ak}|^2 - |t^{(i)}_{ak}|^2 \right] \tag{2.81}$$

$$C = -\frac{2}{\hbar F_a} \mathcal{I}m \, (t_{aa}) \tag{2.82}$$

$$D = \frac{2}{\hbar F_a} \mathcal{R}e \, (t_{aa}) \tag{2.83}$$

$$E_k = e_k + \mathcal{R}e \, (t_{kk}) \tag{2.84}$$

$$\Gamma_k = -2 \, \mathcal{I}m \, (t_{kk}) \, . \tag{2.85}$$

Then the attenuation cross-section becomes

$$\sigma(a) = C + \sum_k \frac{(\Gamma_k/2) B_k + (E - E_k) A_k}{(E - E_k)^2 + (\Gamma_k/2)^2} \tag{2.86a}$$

while the refractivity is

$$n(a) - 1 = \frac{N_a}{2k_a} \left\{ \sum_k \frac{(\Gamma_k/2) A_k - (E - E_k) B_k}{(E - E_k)^2 + (\Gamma_k/2)^2} - D \right\} . \tag{2.87a}$$

Near an isolated resonance one term dominates the summations in Eq. (2.81) and we can write

$$\sigma(a) = C_K + \frac{(\Gamma_K/2)B_K + (E-E_K)A_K}{(E-E_K)^2 + (\Gamma_K/2)^2} \tag{2.86b}$$

$$n(a) - 1 = \frac{N_a}{2k_a}\left\{ \frac{(\Gamma_K/2)A_K + (E-E_K)B_K}{(E-E_K)^2 + (\Gamma_K/2)^2} - D_K \right\} \tag{2.87b}$$

where, with the assumption that all other resoncance widths Γ_N are much smaller than the separation between levels,

$$C_K = C + \sum_{N \neq K} \left\{ \frac{A_N}{E_K - E_N} + \frac{B_N \Gamma_N}{2(E_K - E_N)^2} \right\} \tag{2.88}$$

$$D_K = D + \sum_{N \neq K} \left\{ \frac{B_N}{E_K - E_N} - \frac{A_N \Gamma_N}{2(E_K - E_N)^2} \right\}. \tag{2.89}$$

The incident energy $E \equiv E_a$ must be apportioned between projectile and target. Initially, the target is in a discrete state (typically the ground state) with energy E_I, so that E may be written

$$E = E_I + e_{\text{projectile}} . \tag{2.90a}$$

The projectile energy $e_{\text{projectile}}$ takes a continuum of positive values. For reactions induced by a single incident photon, this expression reads

$$E = E_I + \hbar\omega \ . \tag{2.90b}$$

Thus one obtains, for photons,

$$\sigma(a,\omega) = C_k(\omega) + \frac{(\Gamma_k/2)\,B_k + (\omega-\omega_{kI})\,\hbar A_k}{\hbar^2(\omega-\omega_{kI})^2 + (\Gamma_k/2)^2} \ , \tag{2.91}$$

$$n(a,\omega)-1 = \frac{cN_a}{2\omega}\left\{ \frac{(\Gamma_k/2)\,A_k - (\omega-\omega_{kI})\,\hbar B_k}{\hbar^2(\omega-\omega_{kI})^2 + (\Gamma_k/2)^2} - D_k(\omega)\right\} , \tag{2.92}$$

where $E_k - E_I = \hbar\omega_{kI}$.

The label a is retained as a reminder that these quantities depend on properties other than photon frequency: they depend on initial target-state and on photon polarization.

It should be noted that the matrix element of $(E - H^o - QtQ)^{-1}$ takes the simple form

$$\langle\Phi_k|\,\frac{1}{E - H^o - QtQ}\,|\Phi_k\rangle = \frac{1}{E - e_k - t_{kk}} \tag{2.93}$$

only if Φ_k satisfies Eq. (2.72). As I discuss in the following section, this condition generally requires one to diagonalize the matrix of V between degenerate (or nearly degenerate) states. If this diagonalization is not carried out, the denominator of

Eq. (2.85) no longer retains this simple form; the matrix elements become[80]

$$\langle \Phi_K | \frac{1}{E - H^0 - Q t Q} | \Phi_L \rangle = \frac{[\text{cofactor}(E - H^0 - Q t Q)]_{KL}}{\text{determinant}\ (E - H^0 - Q t Q)} . \tag{2.94}$$

For example, if two levels Φ_K and Φ_L lie close together, Eq. (2.86) gives the elements

$$\langle \Phi_K | \frac{1}{E - H^0 - Q t Q} | \Phi_K \rangle = \frac{1}{E - e_K - t_{KK} - t_{KL}\, \eta(E)} \tag{2.95a}$$

$$\langle \Phi_K | \frac{1}{E - H^0 - Q t Q} | \Phi_L \rangle = \frac{\eta(E)}{E - e_K - t_{KK} - t_{KL}\, \eta(E)} \tag{2.95b}$$

where

$$\eta(E) = \frac{t_{LK}}{E - e_L - t_{LL}} . \tag{2.96}$$

Near the resonance frequency $E = e_K$, the correction to t_{KK} becomes approximately

$$t_{KL}\, \eta(E) \cong \frac{t_{KL}\, t_{LK}}{e_K - e_L} . \tag{2.97}$$

Thus the correction $\eta(E)$ cannot be neglected if the coupling

t_{LK} is large or if the resonances are closely spaced. Mower[77] discusses this point in detail.

It should also be noted that the present approach predicts a resonance width which is a property of the resonance state alone rather than a width which depends on the initial state as well. (In the Weisskopf-Wigner theory[15] the observed width is the sum of widths for initial and final states.) This is because I assume the initial state persisted indefinitely in the past, i.e. has a negligible width. A more refined approach would include the decay of the initial state.

The task of reaction theory is two-fold: first, to provide a realistic parameterization of cross-sections; and second, to offer means of predicting and interpreting the parameters. The preceeding equations are an attempt to fulfill the first task and to connect observed profiles with atomic matrix elements. In the next section I shall address the second task.

III. PERTURBATION THEORY APPLIED TO COLLISIONS

A. Formulation

While Eq. (2.78), like the Lippmann-Schwinger equation, is an "exact" equation, actual calculations require the introduction of approximations; the many-body scattering problem is no more soluble then the many-body Schrödinger equation. Perturbation theory (suitably formulated) has proven quite accurate in conventional calculations of atomic properties, including radiative effects, and one anticipates this accuracy will carry over to scattering problems.

For simplicity, I shall neglect degeneracy for the moment, and will omit identification subscripts on states. This deficiency is removed in section III-C.

We seek a solution to the Schrödinger-like equation

$$Q(H^{o} + V + V\mathcal{G}_{p}V - \mathcal{E})Q\Phi = 0 \tag{3.1}$$

(where $\mathcal{E}$ is a complex number) in a basis of eigenstates of H^{o}:

$$(H^{o} - e)\varphi = 0. \tag{3.2}$$

As a first step, the operator $\mathscr{t} = V\mathscr{G}_p V$ must be expressed in a calculable form. This can be done by use of the expansion

$$\mathscr{G}_p V = \frac{P}{E^+ - H^\circ}\,\mathscr{t}$$

$$= \frac{P}{E^+ - H^\circ} V + \frac{P}{E^+ - H^\circ} V \frac{P}{E^+ - H^\circ} V + \cdots \tag{3.3}$$

The application of conventional Rayleigh-Schrödinger perturbation theory[81] to Eq. (3.1) by use of the expansion

$$\Phi = \varphi^{(0)} + \varphi^{(1)} + \varphi^{(2)} + \cdots \tag{3.4a}$$

$$\mathcal{E} = e + e^{(1)} + e^{(2)} + e^{(3)} + \cdots , \tag{3.4b}$$

and the condition (for states of the same energy)

$$\langle \varphi^{(0)} | \varphi^{(n)} \rangle = \delta_{0n} , \tag{3.5}$$

leads to the sequence of equations:

$$\begin{aligned} 0 = {} & (H^\circ - e)\varphi^{(n)} + (V - e^{(1)})\varphi^{(n-1)} \\ & + \left(V \frac{P}{E^+ - H^\circ} V - e^{(2)}\right)\varphi^{(n-2)} \\ & + \left(V \frac{P}{E^+ - H^\circ} V \frac{P}{E^+ - H^\circ} V - e^{(3)}\right)\varphi^{(n-3)} + \cdots \end{aligned} \tag{3.6}$$

It then follows that, to second order, Φ is given by:

$$\Phi = \varphi^{(0)} + \frac{Q^0}{e-H^0} V \varphi^{(0)} + \frac{Q^0}{e-H^0} V \frac{Q^0}{e-H^0} V \varphi^{(0)} + \frac{Q^0}{e-H^0} V \frac{P}{E^+-H^0} V \varphi^{(0)} \tag{3.7}$$

where $\varphi^{(0)}$ is an eigenstate of the unperturbed Hamiltonian,

$$(H^0 - e)\,\varphi^{(0)} = 0, \tag{3.8}$$

and Q^0 removes the $\varphi^{(0)}$ component of Φ:

$$Q^0 = 1 - |\varphi^{(0)}\rangle\langle\varphi^{(0)}| . \tag{3.9}$$

To second order, $\mathcal{E}$ is

$$\begin{aligned} \mathcal{E} &= \langle\varphi^{(0)}|\; H^0+V \;|\varphi^{(0)}\rangle \\ &\qquad \langle\varphi^{(0)}|\; V \frac{Q^0}{e-H^0} V + V \frac{P}{E^+-H^0} V \;|\varphi^{(0)}\rangle . \end{aligned} \tag{3.10}$$

From the discussion in part I, it is clear that interest in the $\mathscr{T}$ matrix extends beyond the calculation of positions and widths of resonances. Details of resonance profiles depend on the elements of $\mathscr{t}$ between a resonance state Φ and a continuum state ψ. Equations (3.3) and (3.7) give these, to second order, as

$$\langle \psi | t | \Phi \rangle = \langle \psi | V | \varphi^{(0)} \rangle + \langle \psi | V \frac{Q^0}{e-H^0} V | \varphi^{(0)} \rangle + \langle \psi | V \frac{P}{E^+ - H^0} V | \varphi^{(0)} \rangle . \tag{3.11}$$

Third-order corrections to $\mathcal{E}$ and $\langle \psi | t | \Phi \rangle$ come from matrix elements of the operator

$$V \left(\frac{Q^0}{e-H^0} V + \frac{P}{E^+ - H^0} V \right)^2 . \tag{3.12}$$

B. Basis States

At this stage, it is useful to introduce a set of basis states -- eigenstates of H^0 -- and to show how the partition into P and Q may be made.

I shall assume that H^0 is the sum of Hermitian single-particle operators[82] $h(i)$,

$$H^0 = \sum_i h(i) \tag{3.13}$$

whose degenerate eigenstates satisfy the equation

$$(h(i) - \epsilon_\alpha)\, u_\alpha(i) = 0. \tag{3.14}$$

The product of such single-particle states, the <u>product-state</u>

$$u_\alpha(1)\, u_\beta(2) \cdots u_\xi(N), \tag{3.15}$$

is an eigenstate of H^0 with eigenvalue

$$e_a = \epsilon_\alpha + \epsilon_\beta + \cdots + \epsilon_\xi . \tag{3.16}$$

Basis states can be constructed from linear combinations of degenerate product states; an N-particle basis state has the form

$$|a\rangle = \sum (a|\alpha\beta\cdots\xi)\, u_\alpha(1)\, u_\beta(2) \cdots u_\xi(N). \tag{3.17}$$

I shall assume this construction has incorporated the requirements that $|a\rangle$ be symmetric in boson coordinates and antisymmetric in fermion coordinates.[83] The construction may also include the coupling of single-particle angular-momentum, but it does not include configuration mixing. The label a specifies single-particle quantum-numbers and collective quantum-numbers.

Single-particle states fall into two classes, distinguished by their single-particle energies.[84] When ϵ_α is negative, it takes only discrete values; the wave function $u_\alpha(\underset{\sim}{r})$ then falls off exponentially at large distances, and one has a bound single-particle state. When ϵ_α is positive, it can take any value; the wavefunction $u_\alpha(\underset{\sim}{r})$ then describes a wave train at infinity, and one has a continuum single-particle state.

Given a collection of product states, one can recognize those products that are composed entirely of bound single-particle states (to be denoted by labels k, m, or n). I shall call this subset the closed-channel states, and write

$$Q = \sum_n |n\rangle\langle n| \cdot \tag{3.18}$$

The remaining collection of states (to be denoted by labels a, b, c, or d) comprise the open-channel states,

$$P = \mathop{\mathrm{S}}_{c} |c\rangle\langle c| \tag{3.19}$$

Each open-channel state $|c\rangle$ has at least one single-particle continuum-state; each closed-channel state $|n\rangle$ is built from bound single-particle states.

As Part IV will discuss, the inclusion of photon projectiles introduces no fundamental difficulty. Let the index γ stand for frequency, polarization, and propagation vector. Then each free-field photon satisfies an equation of the form

$$(h_{\text{photon}}(\gamma) - \epsilon_\gamma) u_\gamma = 0 \tag{3.20}$$

where $\epsilon_\gamma = \hbar\omega_\gamma$. The Hamiltonian H^o can then be written

$$H^\circ = \sum_i h_{\text{particle}}(i) + \int_\gamma h_{\text{photon}}(\gamma) \equiv H^\circ_{\text{atom}} + H^\circ_{\text{radiation}} \tag{3.21}$$

and the preceding arguments apply. The basis states must now be taken from a photon Fock-space.[85-86] That is, one requires product states with no photons, one photon, two photons,..., etc. The label a on a basis state must now list the number of photons of each type γ that are present in the field, as well as specify the state of the atom.

If we are concerned with processes that occur when a single photon encounters a target, then we can define closed channels as those product states that have no photons; all product states that have one or more photons are then open channels. The sum over continuum states becomes a sum over atomic states and a sum over photon states,

$$\mathop{S}_{c} = \mathop{S}_{\text{atom}} \mathop{S}_{\gamma} , \tag{3.22}$$

while the sum over discrete states and resonance states is simply a sum over atomic quantum-numbers.

C. Resonance States

The zero-order approximation $\varphi^{(0)}$ to the resonance state Φ is, like the basis states, an eigenstate of H^{o}. However, it does not follow that $\varphi^{(0)}$ must be a particular basis state. The basis states are, in general, degenerate. Therefore the zero-order states must be chosen to diagonalize the matrix of V between degenerate states.[87] A partial diagonalization is accomplished by constructing antisymmetrized angular-momentum basis states (Eq. (3.17)), but further configuration degeneracy may still remain.[88] In principle, one can redefine the basis states to coincide with these zero-order states. In practice, it is often useful to retain the original basis states and introduce mixing coefficients:

$$\varphi_K^{(0)} \equiv |K\rangle = \sum_k |k\rangle (k|K) \cdot \tag{3.23}$$

The mixing coefficients $(K|k)$ which connect the zero-order resonance states $|K\rangle$ with the original basis-states $|k\rangle$ are obtained by solving the equations

$$\langle K|V|K'\rangle = 0 \qquad \text{if} \quad K \neq K'$$

$$\langle K|V|K\rangle = \sum_{kk'} (K|k)\langle k|V|k'\rangle (k'|K') \tag{3.24}$$

between degenerate zero-order states. Matrix elements to zero-order states will be denoted by capitals K, L, M, N; elements to the undiagonalized basis states will have lower case labels k, l, m, n.

The first-order correction to $\varphi_K^{(0)}$, as prescribed by Eq. (3.3), is

$$\varphi^{(1)}_K = \sum_n{}' \frac{|n\rangle\langle n|V|K\rangle}{e_k - e_n} = \sum_n{}'\sum_k \frac{|n\rangle\langle n|V|k\rangle(k|K)}{e_k - e_n} . \tag{3.25}$$

Thus the resonance state is, to first order,

$$\Phi_K \cong \varphi^{(0)}_K + \varphi^{(1)}_K = \sum_k (k|K)\left\{|k\rangle + \sum_n{}' \frac{|n\rangle\langle n|V|k\rangle}{e_k - e_n}\right\} . \tag{3.26}$$

The resonance energy, to second order, is

$$\begin{aligned} E_K(E) = e_k + \sum_{kk'} (K|k)(k|K') \Bigg\{ &\langle k|V|k'\rangle \\ &+ \sum_n{}' \frac{\langle k|V|n\rangle\langle n|V|k'\rangle}{e_k - e_n} + \int_d{}' \frac{\langle k|V|d\rangle\langle d|V|k'\rangle}{E - E_d} \Bigg\} \end{aligned} \tag{3.27a}$$

while the resonance width, to second order (using $e^{(3)}$), is

$$\begin{aligned} \Gamma_K(E) = 2\pi \int_c \delta(E - E_c) \sum_{kk'} (K|k)(k'|K) \langle k|V|c\rangle \times \\ \times \Bigg\{ \langle c|V|k'\rangle + 2\mathrm{Re}\sum_n{}' \frac{\langle c|V|n\rangle\langle n|V|k'\rangle}{e_k - e_n} + 2\,\mathrm{Re}\int_d{}' \frac{\langle c|V|d\rangle\langle d|V|k'\rangle}{E - E_d} \Bigg\} . \end{aligned} \tag{3.28a}$$

The appearance of E (the initial energy in the scattering problem) in these expressions for $E_K(E)$ and $\Gamma_K(E)$ means that, as formulated here, the resonance parameters depend on incident energy. However, this dependence may be neglected over a sufficiently small energy interval near $E = e_K$.

In turn, the perturbation equations give the direct-reaction background from the approximations

$$\mathrm{Re}\left[t_{ab}(E)\right] \cong \langle a|V|b\rangle + \int_d{}' \frac{\langle a|V|d\rangle\langle d|V|b\rangle}{E - E_d}\,, \tag{3.29}$$

$$\mathrm{Im}\left[t_{ab}(E)\right] \cong -\pi \int_c \delta(E - E_c)\,\langle a|V|c\rangle\langle c|V|b\rangle\,, \tag{3.30}$$

and the resonance-scattering properties from

$$t_{aK}^{(r)}(E) = \sum_k (K|k)\left\{\langle a|V|k\rangle + \sum_n{}' \frac{\langle a|V|n\rangle\langle n|V|k\rangle}{e_k - e_n} + \int_d{}' \frac{\langle a|V|d\rangle\langle d|V|k\rangle}{E - E_d}\right\}, \tag{3.31a}$$

$$t_{aK}^{(i)}(E) = -\pi \int_c \delta(E - E_c) \sum_k (K|k)\,\langle a|V|c\rangle\langle c|V|k\rangle\,. \tag{3.32a}$$

The preceding expressions simplify slightly if one takes matrix elements to the zero-order resonance-state $|K\rangle$ rather than to the basis states $|k\rangle$. The equations then become:

$$E_k = e_k + \langle k|V|K\rangle + \sum_n \frac{|\langle K|V|n\rangle|^2}{e_k - e_n} + \int'_d \frac{|\langle K|V|d\rangle|^2}{E - E_d}, \tag{3.27b}$$

$$\Gamma_k = 2\pi \int_c \delta(E - E_c)\langle k|V|c\rangle \left\{ \langle c|V|K\rangle + 2\,\mathrm{Re} \sum_n{}' \frac{\langle c|V|n\rangle\langle n|V|k\rangle}{e_k - e_n} + 2\,\mathrm{Re} \int_d \frac{\langle c|V|d\rangle\langle d|V|k\rangle}{E - E_d} \right\}, \tag{3.28b}$$

$$t^{(r)}_{aK} = \langle a|V|K\rangle + \sum_n{}' \frac{\langle a|V|n\rangle\langle n|V|K\rangle}{e_k - e_n} + \int'_d \frac{\langle a|V|d\rangle\langle d|V|K\rangle}{E - E_d}, \tag{3.31b}$$

$$t^{(i)}_{aK} = -\pi \int_c \delta(E - E_c)\langle a|V|c\rangle\langle c|V|K\rangle . \tag{3.32b}$$

To lowest order, the resonance parameters A_K and B_K of Eqs. (2.80) and (2.81) are given by:

$$A_K = \frac{4\pi}{\hbar F_a}\, \mathrm{Re}\left\{ \langle a|V|K\rangle \int_c \delta(E-E_c)\,\langle K|V|c\rangle\langle c|V|a\rangle \right\}, \tag{3.33}$$

$$B_K = \frac{1}{\hbar F_a}\left\{ |\langle a|V|K\rangle|^2 - \pi^2 \left| \int_c \delta(E-E_c)\,\langle a|V|c\rangle\langle c|V|K\rangle \right|^2 \right\}. \tag{3.34}$$

To lowest order, the background for an isolated level (Eqs. (2.88) and (2.89)) comes from[90]

$$C_K = \frac{1}{\hbar F_a}\left\{ 2\pi \int_c \delta(E-E_c)\,|\langle a|V|c\rangle|^2 + \sum_{N\neq K} \frac{\Gamma_N\,|\langle a|V|N\rangle|^2}{(E-E_N)^2} \right\}, \tag{3.35}$$

$$D_K = \frac{2}{\hbar F_a}\left\{ \langle a|V|a\rangle + \int_d' \frac{|\langle a|V|d\rangle|^2}{E-E_d} + \sum_{N\neq K} \frac{|\langle a|V|N\rangle|^2}{E-E_N} \right\}. \tag{3.36}$$

The preceding formulas, taken with Eqs. (2.79)-(2.80) of the previous section, provide a link between observed resonance profiles and calculable matrix elements. With the perturbation-theory approach, each matrix element may be interpreted as the amplitude for a particular type of process.[91] Specifically:

$\langle a\vert V\vert a\rangle$	gives forward elastic scattering,
$\langle a\vert V\vert c\rangle$	describes potential scattering (or direct reactions) from one open channel directly to another open channel,
$\langle a\vert V\vert K\rangle$ or $\langle a\vert V\vert k\rangle$	describes capture from an open channel to a resonance state,
$\langle K\vert V\vert c\rangle$ or $\langle k\vert V\vert c\rangle$	gives the decay of a resonance state into an open channel.

By examining the matrix-element structure of the quantities A_K, B_K, Γ_K, etc. (Eqs. (2.80)) one can picture a sequence of elementary events that "cause" A_K, B_K, Γ_K, etc.

For example, the first approximation to the resonance width is[25]

$$\Gamma_k = 2\pi \int_c \delta(E - E_c) \, |\langle c|V|k\rangle|^2 \, . \tag{3.37}$$

This is the sum of terms $2\pi\delta(E - E_c) \, |\langle c|V|K\rangle|^2$, each of which gives the probability per unit time for decay of the state $\varphi_K^{(0)}$ into a continuum state ψ_c, conserving energy.[92]

The direct-reaction contribution to the attenuation cross-section is

$$C = \frac{2\pi}{\hbar F_a} \int_c \delta(E-E_c)\, |\langle a|V|c\rangle|^2 . \tag{3.38}$$

This expression[21-23] is simply the first Born-approximation for scattering from incident state ψ_a to all possible continuum states ψ_c, conserving energy.[93]

Similarly, the first part of B_K,

$$\frac{2}{\hbar F_a} |\langle a| V | k\rangle|^2 , \tag{3.39}$$

gives the probability for a transition from the discrete resonance state $\varphi_K^{(0)}$ into the continuum ψ_a (or the probability of capture from ψ_a to $\varphi_K^{(0)}$). The parameter A_K, as well as the negative part of B_K, depends on the matrix element

$$\delta(E-E_c)\, \langle a|V|c\rangle . \tag{3.40}$$

This quantity vanishes unless appreciable scattering occurs from the continuum ψ_a into the continuum ψ_c, at the same energy.[94]

One can then see that a finite A_K or negative B_K indicates appreciable continuum scattering. An illustrative example occurs in the profiles of neutron-attenuation cross-sections. Only the s-wave part of an incident neutron beam suffers appreciable elastic scattering: the angular-momentum barrier diminishes contact between the nucleus and higher partial waves. Hence only s-wave resonance-profiles display the marked asymmetry associated with a finite A_K parameter.[95] Figure 2, taken from the work of Peterson, Barshall, and Bockelman,[96] illustrates the striking difference between s-wave and higher partial-wave resonances in the attenuation of neutrons.

IV. PHOTON COLLISIONS

A. The Hamiltonian

As a specific example of the preceding general results, consider an atom interacting with a radiation field.[97] The Hamiltonian for this system splits into four parts:

$$H = H^{o}_{atom} + H^{o}_{rad} + \mathcal{V} + V_{rad} \tag{4.1}$$

$H^{o}_{atom} + \mathcal{V}$ describes the isolated atom, H^{o}_{rad} describes the free radiation-field, and V_{rad} governs the interaction between radiation and the atom.

The "unperturbed" atomic Hamiltonian,

$$H^{o}_{atom} = \sum_{i} h_{electron}(i) , \tag{4.2}$$

is implicitly defined when one chooses a set of single-electron states or <u>orbitals</u>, $u_{\alpha}(i)$. (Typically, these orbitals are hydrogenic or Hartree-Fock orbitals.) Then $\mathcal{V}$ is the remainder of the isolated-atom Hamiltonian. When magnetic interactions and other relativistic effects can be neglected, this Hamiltonian is

$$H^{o}_{\text{atom}} + \mathcal{V} = \sum_{i} \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i} \sum_{j<i} \frac{e^2}{r_{ij}} \tag{4.3}$$

In practice, $\mathcal{V}$ describes part or all of the inter-electron coulomb repulsion; with a more exact atomic Hamiltonian it will include spin-dependent terms.[100]

The radiation field is a collection of photons, each distinguished by an index γ denoting frequency, polarization, and other properties. A photon is characterized by an electric field $\underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r})$ and a magnetic field $\underset{\sim}{\mathcal{H}}_\gamma(\underset{\sim}{r})$, or a vector potential $\underset{\sim}{A}_\gamma(\underset{\sim}{r})$:

$$\underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r}) = -i\frac{\omega_\gamma}{c}\underset{\sim}{A}_\gamma(\underset{\sim}{r}) \, , \qquad \underset{\sim}{\mathcal{H}}_\gamma(\underset{\sim}{r}) = \underset{\sim}{\text{curl}}\, \underset{\sim}{A}_\gamma(\underset{\sim}{r}) \, . \tag{4.4}$$

The free radiation-field has $|\underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r})|^2$ equal to $|\underset{\sim}{\mathcal{H}}_\gamma(\underset{\sim}{r})|^2$, and the Hamiltonian may be written[86,98]

$$H^{o}_{\text{rad}} = \frac{1}{4\pi} \int_{\gamma} \int d\underset{\sim}{r} \, |\underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r})|^2 \equiv \int_{\gamma} h_{\text{photon}}(\gamma) \, . \tag{4.5}$$

Wtih neglect of magnetic interactions, the interaction between photons and electrons may be described by the term[101]

$$V_{\text{rad}} = \sum_{i} \int_{\gamma} e\, \underset{\sim}{r}_i \cdot \underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r}_i) \, . \tag{4.6}$$

B. Photon Fock-Space

The photon Fock-space[85] consists of basis states which have no photons,

$$|n\rangle \equiv |n,0\rangle , \qquad |c\rangle \equiv |c,0\rangle ; \tag{4.7a}$$

states with N_γ photons of type γ,

$$|n, N_\gamma\rangle , \qquad |c, N_\gamma\rangle ; \tag{4.7b}$$

and states where various types of photons are present,

$$|n, N_\gamma \cdots N_{\gamma'} \cdots\rangle , \qquad |c, N_\gamma \cdots N_{\gamma'} \cdots\rangle . \tag{4.7c}$$

Here, and in the following section, labels n and c refer to discrete and continuum <u>atomic</u> <u>states</u>. A state with N_γ identical photons,

$$|N_\gamma\rangle = (u_\gamma)^{N_\gamma} / (N_\gamma !) , \tag{4.8}$$

satisfies the equation

$$(h_{\text{photon}}(\gamma) - \epsilon_\gamma) \, | N_\gamma \rangle = 0 \tag{4.9}$$

with $\epsilon_\gamma = N_\gamma \hbar\omega_\gamma$.

In writing sums over possible states of the system, one must include states of the radiation field. The previous continuum summation, Eq. (3.22), becomes a summation over the atomic continuum and a summation over the photon states:

$$\int_c \longrightarrow \int_c + \int_c \int_\gamma + \sum_n \int_\gamma + \int_c \int_\gamma \int_{\gamma'} + \sum_n \int_\gamma \int_{\gamma'} + \cdots \; . \tag{4.10}$$

We are concerned with collision processes that occur to a target atom in the initial discrete-state $\varphi_I^{(0)}$. For a photon projectile, the incident state ψ_a of preceding sections becomes

$$\psi_a = | I, 1_\gamma \rangle \; . \tag{4.11a}$$

One can then define the closed channels as those discrete atomic states with no photons,

$$\psi_n = |n, 0_\gamma\rangle \equiv |n\rangle . \tag{4.12a}$$

More generally, one may wish to consider processes initiated by N_γ identical photons:[102]

$$\psi_a = |I, N_\gamma\rangle . \tag{4.11b}$$

It is then more appropriate to require that all closed-channel states include a photon factor $|(N-1)_\gamma\rangle$:

$$\psi_n = |n, (N-1)_\gamma\rangle . \tag{4.12b}$$

The operator H^o_{rad} is diagonal in Fock-space, and has the non-zero matrix-elements[86]

$$\langle a, N_\gamma \mid H^o_{rad} \mid a, N_\gamma\rangle = N_\gamma \hbar\omega_\gamma . \tag{4.13}$$

(The continuum label a may be replaced by a discrete state label n.) The operator $\underset{\sim}{\mathcal{E}}_\gamma(\underset{\sim}{r})$ has non-zero matrix-elements only between states that differ by the presence of one photon:[103]

$$\langle b, N_\gamma \mid \boldsymbol{\mathcal{E}}_\gamma(\mathbf{r}) \mid a, (N+1)_\gamma \rangle = -i\sqrt{N_\gamma+1}\,\sqrt{2\pi\hbar c^2\omega_\gamma}\;\langle b|\mathbf{U}_\gamma(\mathbf{r})|a\rangle \qquad (4.14a)$$

$$\langle b, (N+1)_\gamma \mid \boldsymbol{\mathcal{E}}_\gamma(\mathbf{r}) \mid a, N_\gamma \rangle = i\sqrt{N_\gamma+1}\,\sqrt{2\pi\hbar c^2\omega_\gamma}\;\langle b|\mathbf{U}^*_\gamma(\mathbf{r})|a\rangle \qquad (4.14b)$$

(the labels a and b may be replaced by n and m). Here $\mathbf{U}_\gamma(\mathbf{r})$ is a solution to the vector Helmholtz-equation,

$$\mathbf{curl}\;\mathbf{curl}\;\mathbf{U}_\gamma(\mathbf{r}) + \left(\frac{\omega_\gamma}{c}\right)^2 \mathbf{U}_\gamma(\mathbf{r}) = 0 , \qquad (4.15)$$

normalized to satisfy the condition

$$\int d\mathbf{r}\;\mathbf{U}_\gamma(\mathbf{r})\cdot\mathbf{U}^*_{\gamma'}(\mathbf{r}) = \delta_{\gamma\gamma'} . \qquad (4.16)$$

Usually the $\mathbf{U}_\gamma(\mathbf{r})$ fields are chosen as transverse plane-waves. The label γ then specifies the propagation vector $\mathbf{k}$ (with $|\mathbf{k}| = \omega/c$) and polarization $\boldsymbol{\epsilon}$ (with $\mathbf{k}\cdot\boldsymbol{\epsilon} = 0$):

$$\mathbf{U}_{\boldsymbol{\epsilon}\mathbf{k}}(\mathbf{r}) = \boldsymbol{\epsilon}\,\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}} \qquad (4.17)$$

With this choice of normalization, the incident flux F_γ

(assuming one incident photon) and the summation over photon indices become

$$F_{\underset{\sim}{\epsilon}\underset{\sim}{k}} = c, \qquad \mathop{\mathrm{S}}_{\underset{\sim}{\epsilon}\underset{\sim}{k}} = \sum_{\underset{\sim}{\epsilon}} \int k^2 dk \int d\Omega \tag{4.18}$$

where c is the speed of light.

However, atomic transitions occur between states of well-defined parity and total angular momentum. It therefore proves useful to take the $\underset{\sim}{U}_{\gamma}(\underset{\sim}{r})$ fields as transverse multipole-fields[104-108] characterized by frequency ω, parity ($\mathcal{E}$ for electric multipoles, $\mathcal{M}$ for magnetic multipoles) multipole order ℓ, and angular-momentum component μ:

$$\underset{\sim}{U}_{\omega\mathcal{M}\ell\mu}(r,\Omega) = \left[\frac{2}{\pi\ell(\ell+1)}\right]^{1/2} \frac{\omega}{c}\, j_{\ell}\left(\frac{\omega r}{c}\right) \underset{\sim}{L}\, Y_{\ell\mu}(\Omega), \tag{4.19a}$$

$$\underset{\sim}{U}_{\omega\mathcal{E}\ell\mu}(r,\Omega) = \frac{c}{\omega}\,\mathrm{curl}\,\underset{\sim}{U}_{\omega\mathcal{M}\ell\mu}(r,\Omega). \tag{4.19b}$$

where $\underset{\sim}{L}$ is the orbital angular-momentum operator. For such fields one has[108-109] (assuming a single incident photon)

$$F_{\omega\mathcal{E}\ell\mu} = F_{\omega\mathcal{M}\ell\mu} = \frac{\omega^2}{c\pi^2(2\ell+1)}, \qquad \mathop{\mathcal{S}}_{\gamma} = \sum_{\mathcal{E},\mathcal{M}}\sum_{\ell}\sum_{\mu}\int\frac{d\omega}{c} \tag{4.20}$$

and also[105]

$$\underset{\sim}{r}\cdot\underset{\sim}{U}_{\omega\mathcal{M}\ell\mu}(\underset{\sim}{r}) = 0, \tag{4.21a}$$

$$\underset{\sim}{r}\cdot\underset{\sim}{U}_{\omega\mathcal{E}\ell\mu}(\underset{\sim}{r}) = i\left[\frac{2\ell(\ell+1)}{\pi}\right]^{\frac{1}{2}} j_\ell\left(\frac{\omega r}{c}\right)Y_{\ell\mu}(\Omega). \tag{4.21b}$$

Near the atom, where kr << 1, the electric-dipole or $\mathcal{E}1$ field predominates, and matrix elements of the operator

$$\underset{\sim}{U}_{\omega\mathcal{E}1\mu}(\underset{\sim}{r}) \cong \frac{i\omega}{\pi c\sqrt{3}}\,\underset{\sim}{e}_{\mu} \tag{4.22}$$

are responsible for the major transitions. Here $\{\underset{\sim}{e}_{\mu}\} \equiv e_{+1}$, e_0, e_{-1} are unit circular-polarization vectors.[106-107] To simplify the following discussion, I shall consider only $\mathcal{E}1$ photons;[110] the summation over photon states then reduces to a summation over three polarizations and integration over frequency:

$$\mathop{\mathcal{S}}_{\gamma} \rightarrow \sum_{\mu}\int\frac{d\omega}{c}. \tag{4.23}$$

This approximation is equivalent to setting exp(ikr) $\approx$ 1 with plane-wave photons.

It will prove useful to introduce the atomic dipole-moment operator

$$\underset{\sim}{D} = \sum_i \underset{\sim}{r}_i \quad , \qquad D_\mu = \sum_i \underset{\sim}{r}_i \cdot \underset{\sim}{e}_\mu \tag{4.24}$$

and to employ units such that

$$e = \hbar = m = 1 \ , \qquad c = 1/\alpha \cong 137, \tag{4.25}$$

where α is Sommerfeld's Fine-Structure Constant.[111] Only the matrix elements linking one-photon states with two-photon and no-photon states will be required here; these are:

$$\langle a, 1_\gamma \mid V_{rad} \mid b, 0_\gamma \rangle = i\alpha \sqrt{2\omega_\gamma^3/3\pi} \ \langle a \mid D_\mu \mid b \rangle, \tag{4.26a}$$

$$\langle b, 0_\gamma \mid V_{rad} \mid a, 1_\gamma \rangle = -i\alpha \sqrt{2\omega_\gamma^3/3\pi} \ \langle b \mid D_\mu^* \mid a \rangle, \tag{4.26b}$$

$$\langle b, 2_\gamma \mid V_{rad} \mid a, 1_\gamma \rangle = \sqrt{2} \ \langle b, 0_\gamma \mid V_{rad} \mid a, 1_\gamma \rangle . \tag{4.26c}$$

C. Atomic Basis States

The energies of resonance states are determined largely by the atomic Hamiltonian $H^{o}_{\mathrm{atom}} + \mathcal{V}$:

$$E_{K}(\omega) = \langle K | H^{o}_{\mathrm{atom}} | K \rangle + \langle K | \mathcal{V} | K \rangle + \sum_{n}{}' \frac{|\langle K | \mathcal{V} | n \rangle|^{2}}{e_{K} - e_{n}} + \int_{d}{}' \frac{|\langle K | \mathcal{V} | d \rangle|^{2}}{E_{a} - E_{d}} . \tag{4.27}$$

Radiative corrections, such as the Lamb shift, are small and will be neglected here.[111] This expression applies both to autoionizing and non-autoionizing states.

The quantity $E_{K}(\omega)$ depends slightly on excitation conditions (the incident-photon energy ω) through the occurrence of $E_{a} = E_{I} + \omega$ in the last summation. For photons near the resonance energy $\omega \cong \omega_{KI}$, one may substitute e_{K} or E_{K} for E_{a} in this sum, and so recover the usual second-order perturbation expression.

In principle, the task of constructing autoionizing states does not differ significantly from the familiar task of constructing ordinary excited states. In an isolated atom, the major portion of $\mathcal{V}$ comes from the inter-electron Coulomb repulsion, possibly modified by an effective central-field potential.

Additional smaller magnetic interactions, such as the spin-orbit interaction, may also need to be considered.

These remarks suggest[113] that one should choose the atomic basis states to be eigenstates of $\underset{\sim}{S}^2$, the total spin; $\underset{\sim}{L}^2$, the total orbital angular momentum; $\underset{\sim}{J}^2$, the total angular momentum; and $J_z = J_o$, one component of $\underset{\sim}{J}$.

Many treatises discuss the construction of bound many-particle angular-momentum states (<u>coupled states</u>) from products of single-particle states (or <u>orbitals</u>).[114] I shall assume the orbitals have the conventional form

$$u_{\epsilon\mu\ell m}(i) = R_{\epsilon\ell}(r_i)\, \chi_\mu(\underset{\sim}{s}_i)\, Y_{\ell m}(\Omega_i) \tag{4.28}$$

where $Y_{\ell m}(\Omega)$ is a spherical harmonic, $\chi_\mu(\underset{\sim}{s})$ is a spin-$\frac{1}{2}$ function, and $R_{\epsilon\ell}(r)$ is a radial function. When ϵ is negative (so that $u_{\epsilon\mu\ell m}(i)$ describes a bound orbital), it takes only selected discrete values; $R_{\epsilon\ell}(r)$ may then be written $R_{n\ell}(r)$, where n is an integer. I shall assume the bound functions satisfy the condition

$$\int r^2 dr \; R_{n\ell}(r)\, R_{n'\ell'}(r) = \delta_{nn'} \quad , \tag{4.29a}$$

although orthogonality is not essential. When ϵ is positive, it can take a continuum of values. I shall assume the continuum functions satisfy the energy-normalization condition

$$\int r^2 dr \; R_{\epsilon\ell}(r) \, R_{\epsilon'\ell}(r) = \delta(\epsilon - \epsilon') \tag{4.29b}$$

and that they are orthogonal to the bound functions,

$$\int r^2 dr \; R_{\epsilon\ell}(r) \, R_{n\ell}(r) = 0. \tag{4.30}$$

The expansion coefficients of Eq. (3.17), which connect a coupled state with uncoupled product functions, are products of vector-coupling (Clebsch-Gordan) coefficients;[114-115] the single label K, hitherto used to identify the set of quantum number labels, must now be replaced by labels KSLJM:

$$(K \,|\, \alpha \cdots \beta) \longrightarrow (KSLJM \,|\, n\ell m\mu \cdots n'\ell' m'\mu'). \tag{4.31}$$

To first order, these states have energies given by diagonal matrix elements of $H^{o}_{\text{atom}} + v$:

$$\begin{aligned} E_{KSLJM} = {} & \langle KSLJM \,|\, H^{o}_{\text{atom}} \,|\, KSLJM \rangle \\ & + \langle KSLJM \,|\, v \,|\, KSLJM \rangle. \end{aligned} \tag{4.32}$$

If H^{o}_{atom} is independent of spin and if the magnetic-interaction contributions to $\mathcal{V}$ can be ignored, this energy is the so-called "term-energy,"[113] independent of J as well as M:

$$E_{KSL} = \frac{\langle KL \| H^{o}_{atom} \| KL \rangle}{\sqrt{2L+1}} + \frac{\langle KSL \| \mathcal{V} \| KSL \rangle}{\sqrt{2S+1}\,\sqrt{2L+1}} . \qquad (4.33)$$

Here I have employed the reduced matrix[116] of a scalar operator,[117]

$$\langle JM | \mathcal{O} | J'M' \rangle = \frac{\langle J \| \mathcal{O} \| J \rangle}{\sqrt{2J+1}} \delta_{JJ'} \delta_{MM'} . \qquad (4.34)$$

However, when one considers excited states of heavy atoms, the fine-structure splitting of different J-levels can no longer be ignored. One then employs the formula

$$E_{KSLJ} = E_{KSL} + \frac{\langle KSLJ \| \mathcal{V}' \| KSLJ \rangle}{\sqrt{2J+1}} \qquad (4.35)$$

to account for effects of the spin-orbit interaction $\mathcal{V}'$.

Once one has constructed such coupled states of an N-electron atom, one can readily construct (N + 1)-electron states by coupling an additional orbital onto a "core" of N electrons. When electrostatic interactions dominate, one follows the Russell-Saunders prescription[113] to construct states of the form

$$|(S_oL_o)n\ell\ SLJM\rangle \tag{4.36a}$$

where S_oL_o refers to the core, and $n\ell$ refers to the added orbital.[118] However, when the fine-structure splitting of the core becomes appreciable and the added orbital is highly excited, it is more appropriate to use the so-called J-K coupling scheme[119-120] (also called $J\ell$ coupling[121]):

$$|(S_oL_oJ_o)n\ell[K]JM\rangle\ . \tag{4.36b}$$

In vector language, the orbital angular-momentum ℓ has been coupled onto J_o to form K, then the spin $\frac{1}{2}$ has been coupled onto K to form J. Such a coupling scheme becomes particularly appropriate as one examines higher terms in a Rydberg series progressing toward a series limit in a heavy atom; for example, the two series

$$({}^2P_{1/2})n\ell\ , \qquad ({}^2P_{3/2})n\ell\ .$$

The construction of continuum angular-momentum states proceeds in the same way, since continuum orbitals differ from bound orbitals only through their radial function. Conventional coupling procedures then provide a Russell-Saunders continuum,

$$|(S_0 L_0)\epsilon\ell \quad SLJM\rangle \tag{4.37a}$$

or a J-K continuum,

$$|(S_0 L_0 J_0)\epsilon\ell\,[K]\,JM\rangle . \tag{4.37b}$$

The choice of a coupling scheme is largely a matter of convenience, since the two schemes are related by a unitary transformation.[119-120]

D. Resonance Widths

Since the perturbation Hamiltonian $V = V_{rad} + \mathcal{V}$ has been separated into two contributions, the resonance width $\Gamma_K = -2\pi\, \mathcal{I}m[t_{KK}]$ also splits into two parts: a radiative-decay width $\Gamma_K^{(rad)}$, and an electron-decay or autoionizing width $\Gamma_K^{(elec)}$. To lowest order, the radiative width for $\mathcal{E}1$ transitions is (from Eqs. (4.26))

$$\Gamma_K^{(rad)}(\omega) = 2\pi \sum_n \int_\gamma \delta(E_I+\omega-E_n-\omega_\gamma)\left(\frac{2\alpha^2\omega_\gamma^3}{3\pi}\right)|\langle K|D_\gamma|n\rangle|^2 + 2\pi \int_c \int_\gamma \delta(E_I+\omega-E_c-\omega_\gamma)\left(\frac{2\alpha^2\omega_\gamma^3}{3\pi}\right)|\langle K|D_\gamma|c\rangle|^2, \tag{4.38}$$

while the autoionizing width is

$$\Gamma_K^{(elec)}(\omega) = 2\pi \int_c \delta(E_I+\omega-E_c)\,|\langle K|\mathcal{V}|c\rangle|^2. \tag{4.39}$$

As usual, $|n\rangle$ and $|c\rangle$ denote discrete and continuum atomic basis-states respectively.

The radiative width expresses the possibility that the resonance state $\varphi_K^{(0)}$ will decay to some other atomic state, either discrete or continuum, with the emission of a photon.

The radiative width is finite for all excited bound states, since it is always possible to satisfy energy conservation in photon decay to a lower-lying bound state, if one accounts for higher electric- and magnetic-multipole radiation and for multi-photon decay.

The autoionizing width expresses the possibility for an energy-conserving decay to an ionized state plus a free electron; this condition can be met only when a level lies above the first ionization-limit.

a. Radiative widths[122]

To write the radiative width in a more familiar form, we can employ angular-momentum states. The sums over photon polarization, $\mu = -1, 0, +1$, and magnetic quantum-number $M = -J, \ldots, +J$, are then readily carried out with the aid of the Wigner-Eckart theorem:[106-107]

$$\sum_{\mu} \sum_{M_n} |\langle k\, J_k\, M_k \,|\, D_\mu \,|\, n\, J_n\, M_n \rangle|^2 = \frac{|\langle k\, J_k \,\|\, \underset{\sim}{D} \,\|\, n\, J_n \rangle|^2}{2J_k+1} \equiv \frac{|\langle k \,\|\, \underset{\sim}{D} \,\|\, n \rangle|^2}{g_k} . \qquad (4.40)$$

Here I have introduced the statistical weight $g_K \equiv 2J_K + 1$.

The square of the reduced matrix element $\langle K \| \underset{\sim}{D} \| n \rangle$ is often denoted by $\underset{\sim}{S}(K,n)$, the transition strength of Condon and Shortley:[113]

$$\underset{\sim}{S}(K,n) = |\langle K \| \underset{\sim}{D} \| n \rangle|^2 , \tag{4.41}$$

Summation over the energy of the emitted photon then yields the formula

$$\begin{aligned} \Gamma_K^{(rad)}(\omega) &= \frac{4\alpha^3}{3} \sum_{E_n < E_I + \omega} (\omega_{In} + \omega)^3 \frac{|\langle K \| \underset{\sim}{D} \| n \rangle|^2}{g_K} \\ &+ \frac{4\alpha^3}{3} \int_{E_c < E_I + \omega} (\omega_{Ic} + \omega)^3 \frac{|\langle K \| \underset{\sim}{D} \| c \rangle|^2}{g_K} . \end{aligned} \tag{4.42}$$

The sums over final states $|n\rangle$ or $|c\rangle$ are such that $\omega_{In} \equiv E_I - E_n$ and $\omega_{Ic} \equiv E_I - E_c$ are positive. The sums include all states that lie below E_K in energy, and those with energy up to $E_I + \omega$.

The preceding results presume that the incident state has only a single incident photon. The resonance state $\varphi_K^{(0)}$ then has no photons. For intense beams of radiation, one may consider an N_γ-photon incident state $|I,N_\gamma\rangle$. The radiative width for the resonance state $|K,(N-1)_\gamma\rangle$ then becomes proportional to N_γ, according to Eqs. (4.14). This proportionality expresses the fact that, in an intense field, induced transitions as well as spontaneous transitions will deplete an excited state. The intense radiation shortens the lifetime of the excited state, and thereby increases the width.

Near the resonance frequency $\omega = \omega_{KI}$, the radiative width takes the familiar form of the sum of the Einstein transition-probabilities from discrete state $\varphi_K^{(0)}$ to all lower-lying states, both discrete and continuum: that is, the natural width is the inverse of the lifetime τ_K of the excited state:[17]

$$\Gamma_K^{(rad)}(\omega_{KI}) \equiv \gamma_K \equiv (\tau_K)^{-1} = \sum_{E_n<E_K} \frac{4}{3}(\alpha\omega_{Kn})^3 \frac{|\langle K\|\underset{\sim}{D}\|n\rangle|^2}{g_K} + \int_{E_c<E_K} \frac{4}{3}(\alpha\omega_{Kc})^3 \frac{|\langle K\|\underset{\sim}{D}\|c\rangle|^2}{g_K}. \qquad (4.43)$$

However, away from resonance, the frequency dependence of $\Gamma_K(\omega)$ becomes significant.[123] For example, when $\varphi_K^{(0)}$ is the lowest-lying excited state and $\varphi_I^{(0)}$ is the ground state, the radiation width becomes

$$\Gamma_K^{(rad)}(\omega) = \frac{4}{3}(\alpha\omega)^3 \frac{|\langle K\|\underset{\sim}{D}\|I\rangle|^2}{g_K} = \left(\frac{\omega}{\omega_{KI}}\right)^3 \gamma_K . \qquad (4.44)$$

If we introduce the oscillator strength for bound-bound absorption[124]

$$f_{IK} = \frac{2}{3}\,\omega_{KI}\,\frac{|\langle I \| \underset{\sim}{D} \| K\rangle|^2}{g_I} = -\frac{g_K}{g_I}\,f_{KI} \tag{4.45}$$

and the oscillator strength for bound-free absorption,

$$\frac{df_{Ic}}{dE_c} = \frac{2}{3}\,\omega_{cI}\,\frac{|\langle I \| \underset{\sim}{D} \| c\rangle|^2}{g_I}\,, \tag{4.46}$$

the radiative width at resonant frequency may be written[125]

$$\begin{aligned}\gamma_K &= -\sum_{E_n<E_K} 2\alpha\,(\alpha\omega_{Kn})^2 f_{Kn} - \int_{E_c<E_K} 2\alpha\,(\alpha\omega_{Kc})^2\,\frac{df_{Kc}}{dE_c} \\ &= 2\alpha\left\{\sum_{E_n<E_K}(\alpha\omega_{Kn})^2\,\frac{g_n}{g_K}\,f_{nK} + \int_{E_c<E_K}(\alpha\omega_{Kc})^2\,\frac{g_c}{g_K}\,\frac{df_{cK}}{dE_c}\right\}.\end{aligned} \tag{4.47}$$

In general, the width is the sum of oscillator strengths to several lower-lying states. However, the radiative width of the lowest-lying excited state, at resonant frequency, is simply[126]

$$\begin{aligned}\gamma_K &= \frac{4}{3}\,(\alpha\omega_{KI})^3\,|\langle K \| \underset{\sim}{D} \| I\rangle|^2 \\ &= -2\alpha^3\,(\omega_{KI})^2\,f_{KI} = -\frac{8\pi^2\alpha}{(\lambda_{KI})^2}\,f_{KI}\,.\end{aligned} \tag{4.48}$$

Far below this resonance, $\omega << \omega_{KI}$, the width of this lowest state becomes

$$\Gamma_K^{(rad)}(\omega) = - \frac{2(\alpha\omega)^3 f_{KI}}{\omega_{KI}} \tag{4.49}$$

b. Electron widths

To lowest order, the electron width is

$$\Gamma_K^{(elec)}(\omega) = 2\pi \int_c \delta(E_I + \omega - E_c) \, |\langle K | v | c \rangle|^2 . \tag{4.50}$$

In the next approximation, the width is

$$\Gamma_K^{(elec)}(\omega) = 2\pi \int_c \delta(E_I + \omega - E_c) \langle K | v | c \rangle \left\{ \langle c | v | K \rangle + \right.$$
$$\left. + \sum_n \frac{\langle c | v | n \rangle \langle n | v | K \rangle}{e_K - e_n} + \int_d \frac{\langle c | v | d \rangle \langle d | v | K \rangle}{E - E_d} \right\} . \tag{4.51}$$

Thus, the autoionizing width is governed by the matrix element

$$\delta(E_I + \omega - E_c) \langle K | v | c \rangle \tag{4.52a}$$

which describes the autoionizing transition from the excited state $\varphi_K^{(0)}$ to a continuum state ψ_c whose energy is $E_c = E_I + \omega$.

In the Russell-Saunders coupling scheme, these elements take the form

$$\delta(E_I+\omega-E_c)\,\langle \alpha\, SLJM\,|\,\mathcal{V}\,|\,\alpha'(S_0L_0)\,\epsilon\ell\;\, S'L'J'M'\rangle . \tag{4.52b}$$

When external fields are absent, the largest part of $\mathcal{V}$ comes from the inter-electron coulomb repulsion. The non-zero matrix elements then become

$$\delta(E_I+\omega-E_c)\,\frac{\langle \alpha SL\,\|\,\mathcal{V}\,\|\,\alpha'(S_0L_0)\,\epsilon\ell\;\, SL\rangle}{\sqrt{2S+1}\,\sqrt{2L+1}} . \tag{4.52c}$$

From this expression, one obtains White's[127] selection rules for autoionizing transitions:

$$\Delta S=0,\quad \Delta L=0,\quad \Delta J=0,\quad \Delta\text{parity}=0. \tag{4.53}$$

That is, autoionization occurs when an excited state can mix with a continuum state having the same values for S, L, J, and parity.

With energy-normalized radial functions, the autoionizing width in Russell-Saunders coupling is

$$\Gamma_k^{(elec)}(\omega) \equiv \Gamma_k^{(elec)}(\epsilon) = \frac{2\pi}{(2S+1)(2L+1)} \sum |\langle kSL \| v \| (\bar{S}_0\bar{L}_0)\epsilon\bar{\ell}SL\rangle|^2 \tag{4.54}$$

where the summation goes over barred quantum-numbers, and the continuum energy ϵ satisfies the condition

$$\epsilon = E_I + \omega - E_{\bar{S}_0\bar{L}_0} . \tag{4.55}$$

Not all of the excited states whose energy lies above the first ionization limit can satisfy these requirements. For example, the (3p3d) $^1D^o$ term of Mg I, observed by Paschen,[128] lies above the 3s $\epsilon\ell'$ ionization limit. However, there is no (3s $\epsilon\ell$) $^1D^o$ continuum of odd parity with which the (3p3d) $^1D^o$ can mix. Consequently, the (3p3d) $^1D^o$ has only a slight autoionizing probability, and the widths of spectral lines originating in this term are comparable to widths of other non-autoionizing lines. Other examples have been given in refs. 127.

The form of the matrix elements required for the calculation of autoionizing widths is identical with that of the matrix elements required for calculating the energy of an ordinary excited state, apart from the occurrence of a continuous index ϵ in place of a discrete quantum-number n. Thus the widths can be expressed as the sum of squares of various Slater-type integrals, including both "exchange" and "direct" type integrals. The coefficients of these integrals, giving the angular dependence of the matrix element, can be obtained by use of standard procedures.[115]

E. Resonance Parameters

Equation (2.91) gave the resonant part of the diagonal elements of $\mathcal{J}$:

$$\frac{2\,T_{aa}(\omega)}{F_a} = \frac{B_K(\omega) - i\,A_K(\omega)}{\omega_{IK} + \omega + i\left(\Gamma_K(\omega)/2\right)}, \tag{4.56}$$

where the resonance parameters are

$$A_K(\omega) = -4\left\{ t_{aK}^{(\sigma)}(\omega)\, t_{Ka}^{(i)}(\omega) \right\} / F_a , \tag{4.57a}$$

$$B_K(\omega) = 2\left\{ \left| t_{aK}^{(\sigma)}(\omega)\right|^2 - \left| t_{aK}^{(i)}(\omega)\right|^2 \right\} / F_a . \tag{4.57b}$$

With incident $\mathcal{E}1$ radiation, the first approximation to $t_{Ka}^{(i)}(\omega)$ is

$$t_{Ka}^{(i)}(\omega) = i\sqrt{\frac{2\pi\alpha^2\omega^3}{3}} \int_c \delta(E_I + \omega - E_c)\, \langle K|v|c\rangle \langle c|\, D_\mu\, |I\rangle . \tag{4.58}$$

This quantity vanishes unless the resonance state mixes, through the matrix element $\langle K|v|c\rangle$, with a continuum atomic state of energy $E_c = E_I + \omega$. Near the resonance frequency $\omega = \omega_{KI}$ this condition means $E_c = E_K$. That is, $t_{Ka}^{(i)}$ vanishes unless the discrete state $\varphi_K^{(0)}$ can autoionize.

The first approximation to $t_{aK}^{(r)}(\omega)$, for $\mathcal{E}1$ radiation, is

$$t_{aK}^{(r)}(\omega) = i\sqrt{\frac{2\alpha^2\omega^3}{3\pi}}\ \langle I \mid D_\mu \mid K \rangle . \tag{4.59}$$

This quantity expresses the amplitude for a radiative transition between the ground state $\varphi_I^{(0)}$ and the discrete excited-state $\varphi_K^{(0)}$.

From these expressions, it follows that the resonance parameters are:

$$A_K(\omega) = 8\pi^2(\alpha\omega)\ \langle I \mid D_\mu \mid K \rangle \int_c \delta(E_I + \omega - E_c)\ \langle K \mid v \mid c \rangle \langle c \mid D_\mu \mid I \rangle , \tag{4.60a}$$

$$B_K(\omega) = 4\pi(\alpha\omega)\left\{ \left|\langle K \mid D_\mu \mid I \rangle\right|^2 - \pi^2 \left| \int_c \delta(E_I + \omega - E_c)\langle K \mid v \mid c \rangle \langle c \mid D_\mu \mid I \rangle \right|^2 \right\} . \tag{4.60b}$$

For autoionizing transitions, in which $\Gamma_K \approx \Gamma_K^{(elec)}$, the parameters of Fano and Cooper,[45] discussed in Appendix A, are

$$q = \frac{t_{aK}^{(r)}}{t_{aK}^{(i)}} = \frac{\langle I \mid D_\mu \mid K \rangle}{\pi \int_c \delta(E_I + \omega - E_c)\langle I \mid D_\mu \mid c \rangle \langle c \mid v \mid K \rangle} , \tag{4.61a}$$

$$\rho^2 \equiv \frac{\left| t^{(i)}_{Ka} \right|^2}{\mathcal{I}m\left(t_{KK}\right)\,\mathcal{I}m\left(t_{aa}\right)}$$

$$= \frac{\left| \sum_c \delta(E_I+\omega-E_c)\langle K|D_\mu|c\rangle\langle c|\mathcal{V}|K\rangle \right|^2}{\sum_{c'} \delta(E_I+\omega-E_{c'})\,|\langle K|D_\mu|c'\rangle|^2 \;\sum_{c''} \delta(E_I+\omega-E_{c''})\,|\langle K|\mathcal{V}|c''\rangle|^2} \,. \tag{4.61b}$$

The parameters q and ρ^2 depend on frequency only through the variation of the continuum wavefunctions with energy. This dependence should be slight over the resonance.

For most purposes, one deals with target atoms whose magnetic sublevels are degenerate and equally populated. One then wishes a cross-section or refractivity that is <u>summed</u> over magnetic quantum-numbers M_K of the resonance states ($g_K = 2J_K + 1$ sublevels) and <u>averaged</u> over both the photon polarization μ (3 values) and the magnetic quantum-number M_I of the initial atom ($g_I = 2J_I + 1$ possible values). This average yields the resonant term

$$\overline{\left(\frac{2\,T_{aa}}{\Gamma_a}\right)} = \frac{\bar{B}_K + i\,\bar{A}_K}{\omega_{IK} + \omega + i\,(\Gamma_K/2)}\,, \tag{4.62}$$

where

$$\bar{A}_k(\omega) = \frac{8}{3}\frac{\pi^2(\alpha\omega)}{g_I} \mathop{\displaystyle\int\!\!\!\!\!\!\sum}_c \delta(E_I + \omega - E_c) \sum_{M_I \mu M_k} \langle I | D_\mu | k \rangle \langle k | v | c \rangle \langle c | D_\mu | I \rangle , \tag{4.63}$$

$$\bar{B}_k(\omega) = \frac{4\pi}{3}(\alpha\omega) \left\{ \frac{|\langle I \| D \| k \rangle|^2}{g_I} - \frac{\pi^2}{g_I} \sum_{M_I \mu M_k} \left| \mathop{\displaystyle\int\!\!\!\!\!\!\sum}_c \delta(E_I + \omega - E_c) \langle k | v | c \rangle \langle c | D_\mu | I \rangle \right|^2 \right\} . \tag{4.64}$$

F. Background

The resonance profiles are superposed on a continuum background which is the combined effect of distant resonances and direct-scattering processes (Eqs. (2.88)-(2.89) or (3.35)-(3.36)).

Autoionizing lines overlie a photoionization continuum described by

$$C(\omega) = -\frac{2}{F_a}\,\mathrm{Im}\left[t_{aa}(\omega)\right] = \frac{6\pi^3}{\alpha\omega^2}\int_c \delta(E_I+\omega-E_c)\,\frac{2\alpha^2\omega^3}{3\pi}\,\left|\langle I|D_\mu|c\rangle\right|^2. \tag{4.65}$$

Averaged over μ, this yields the continuum-background cross-section,

$$\begin{aligned}\overline{C}(\omega) &= \frac{4}{3}\pi^2(\alpha\omega)\int_c \delta(E_I+\omega-E_c)\,\frac{|\langle I\|D_\mu\|c\rangle|^2}{g_I}\,. \\ &= 2\pi^2\alpha\int_c \frac{df_{Ic}}{dE_c}\,.\end{aligned} \tag{4.66}$$

The background for ordinary absorption lines comes from the second term of Eq. (3.35), which contributes

$$\overline{C}_K = \overline{C} + \frac{2}{3}\pi\alpha\omega\sum_{N\neq K}\frac{|\langle I\|D\|N\rangle|^2\;\Gamma_N(E_K)}{g_I\,(\omega_{KN})^2}\,. \tag{4.67}$$

The background refractivity is given by the second and third terms of Eq. (3.36). The summation over continuum states comprises states with no photons (these must therefore be continuum atomic-states) and states with two identical photons (which may have either discrete or continuum atomic-states). The result is[129]

$$D_K(\omega) = 4\pi\alpha\omega\left\{ \int_d' \frac{|\langle I|D_\mu|d\rangle|^2}{E_I+\omega-E_d} + \int_d' \frac{|\langle I|D_\mu|d\rangle|^2}{E_I+\omega-(E_d+2\omega)} \right.$$

$$\left. + \sum_N \frac{|\langle I|D_\mu|N\rangle|^2}{E_I+\omega-(E_N+2\omega)} + \sum_{N\neq K} \frac{|\langle I|D_\mu|N\rangle|^2}{E_I+\omega-E_N} \right\} . \qquad (4.68)$$

The single term with N = K in the third summation contributes only a negligible portion of D_K, so it may be dropped. The average background then becomes the well-known Sellmeier formula,[6]

$$\bar{n}(\omega) - 1 = -\frac{N_a}{2\alpha\omega}\bar{D}_K(\omega)$$

$$= 2\pi N_a \int_d' \frac{df_{Id}/d\varepsilon_d}{(\omega_{Id})^2-\omega^2} + 2\pi N_a \sum_{N\neq K} \frac{f_{IN}}{(\omega_{IN})^2-\omega^2} . \qquad (4.69)$$

G. Special Cases

a. Ordinary lines

It is instructive to apply these results to the prediction or ordinary (non-autoionizing) line-profiles. In the absence of autoionization, the resonance parameters of Eq. (4.57) become

$$\bar{A}_k(\omega) = 0 \; , \tag{4.70}$$

$$\bar{B}_k(\omega) = \frac{4\pi}{3}(\alpha\omega)\frac{|\langle I|\underset{\sim}{D}|K\rangle|^2}{g_I} = 2\pi\alpha\left(\frac{\omega}{\omega_{kI}}\right) f_{IK} \; . \tag{4.71}$$

These expressions then yield the familiar results for refractivity,[59–60]

$$\bar{n}(\omega) - 1 = \frac{\pi N_e}{\omega_{kI}} \cdot \frac{(\omega_{kI}-\omega) f_{IK}}{(\omega_{kI}-\omega)^2 + (\Gamma_k(\omega)/2)^2} \; , \tag{4.72}$$

and for the attenuation cross-section

$$\bar{\sigma}(\omega) = \frac{\omega}{\omega_{kI}} \cdot \frac{\pi f_{Ik}\,\Gamma_k(\omega)}{(\omega_{kI}-\omega)^2 + (\Gamma_k(\omega)/2)^2} \; . \tag{4.73}$$

Equations (4.72) and (4.73) describe only the portion of $\bar{n}(\omega)$ or $\bar{\sigma}(\omega)$ that comes from a particular resonance. Additional contributions come from all other resonances, as well as from a background of direct reactions. For the lowest-lying resonant state the cross section may also be written

$$\bar{\sigma}(\omega) = \frac{2\pi}{(\alpha\omega)^2}\,\frac{g_K}{g_I}\,\frac{(\Gamma_K/2)^2}{(\omega_{KI}-\omega)^2 + (\Gamma_K/2)^2}. \tag{4.74}$$

Thus, the attenuation cross-section for the so-called "resonance-line" of an atom, at the resonant frequency, takes the remarkably simple value[130]

$$\bar{\sigma}(\omega_{KI}) = \frac{2\pi}{(\alpha\omega_{KI})^2}\,\frac{g_K}{g_I} = \frac{(\lambda_{KI})^2}{2\pi}\,\frac{g_K}{g_I}, \tag{4.75}$$

while the integral over the absorption profile is approximately

$$\int \bar{\sigma}(\omega)\,d\omega \cong 2\pi^2\alpha f_{IK} = \frac{(\lambda_{KI})^2}{4}\,\frac{g_K}{g_I}\,\gamma_K. \tag{4.76}$$

For wavelengths much longer than the "resonance-line," $\omega << \omega_{KI}$ and $\Gamma_K(\omega) \approx 2\alpha\omega^3 f_{IK}/\omega_{IK} << \omega_{KI}$, the cross section takes the familiar Rayleigh-scattering[131] frequency-dependence

$$\bar{\sigma}(\omega) = 4\pi(\alpha f_{IK})^2\,\frac{g_K}{g_I}\left(\frac{\omega}{\omega_{IK}}\right)^4. \tag{4.77}$$

b. Double excitations

Since autoionizing levels lie above an ionization limit, the zero-order resonance state $\varphi_K^{(0)}$ is doubly excited: it differs from the zero-order ground state in two orbitals. Photon transitions from the ground state to an autoionizing state involve a two-electron jump. If the basis orbitals are orthogonal, the matrix element $\langle I|D_\mu|K\rangle$ vanishes, and Eq. (4.59) must be replaced by the more accurate equation

$$
\begin{aligned}
t_{aK}^{(a)}(\omega) = i\sqrt{\frac{2\alpha^2\omega^3}{3\pi}}\Bigg\{ & \langle I|D_\mu|k\rangle \\
& + \sum_n \frac{\langle I|D_\mu|n\rangle\langle n|v|k\rangle + \langle I|v|n\rangle\langle n|D_\mu|k\rangle}{e_k - e_n} \\
& + \int_d \frac{\langle I|D_\mu|d\rangle\langle d|v|k\rangle + \langle I|v|d\rangle\langle d|D_\mu|k\rangle}{(E_I+\omega) - E_d}\Bigg\}.
\end{aligned}
\tag{4.78}
$$

When configuration mixing is slight, $t_{aK}^{(r)}$ is negligibly small, and the profile parameters become

$$
A_k \cong 0, \tag{4.79}
$$

$$
\begin{aligned}
B_k &\cong -\frac{2}{F_a}\left|t_{ak}^{(i)}\right|^2 \\
&= 4\pi^3(\alpha\omega)\left|\int_c \delta(E_I+\omega-E_c)\langle k|v|c\rangle\langle c|D_\mu|I\rangle\right|^2.
\end{aligned}
\tag{4.80}
$$

Such resonances appear as symmetrical transmission windows.

c. Zero-order mixing

The preceding formulas were given in terms of the zero-order states $\varphi_K^{(0)}$. Since these states may be mixtures of configurations, it is useful to rewrite the formulas in terms of basis states rather than zero-order states. The resonance quantities then become, to lowest order:

$$E_K = e_k + \sum_{kk'} (K|k)\,(k'|K)\,\langle k'|V|k\rangle\,, \tag{4.81}$$

$$\Gamma_K^{(rad)} \cong \frac{4}{3}\,\frac{(\omega_{Kn})^3}{g_K} \sum_n \left|\,(K|k)\,\langle k\|\underset{\sim}{D}\|n\rangle\right|^2, \tag{4.82}$$

$$\Gamma_K^{(elec)} \cong 2\pi \int_c \delta(E_I+\omega-E_c)\,\left|\,(K|k)\,\langle k|V|c\rangle\right|^2, \tag{4.83}$$

$$t_{aK}^{(\lambda)} \cong i\sqrt{\frac{2\pi\alpha^2\omega^3}{3}} \int_c \delta(E_I+\omega-E_c)\,\langle I|D_\mu|c\rangle \sum_k \langle c|V|k\rangle\,(k|K)\,, \tag{4.84}$$

$$t_{ak}^{(i)} \cong i\sqrt{\frac{2\pi\alpha^2\omega^3}{3\pi}} \sum_{k} (K|k)\langle I \,|\, D_\mu \,|\, k\rangle . \tag{4.85}$$

The zero-order mixing-coefficients $(K|k)$ may significantly affect predictions. For example, the Z-expansion theory[89] regards the 2snp and the 2pns configurations of helium as degenerate to zero-order. The theory prescribes zero-order states of the form

$$\begin{gathered} |2n^{\pm}\rangle = \alpha\,|2s\,np\rangle \pm \beta\,|2p\,ns\rangle \\ \alpha^2 + \beta^2 = 1 \end{gathered} \tag{4.86}$$

where α and β are the zero-order mixing-coefficients. The autoionizing widths to the 1sεp continuum are

$$\Gamma_{2n+}^{(elec)}(\epsilon) = 2\pi \left| \alpha \langle 2snp|v|1s\epsilon p\rangle + \beta \langle 2p\,ns|v|1s\epsilon p\rangle \right|^2 \tag{4.87a}$$

$$\Gamma_{2n-}^{(elec)} = 2\pi \left| \alpha \langle 2snp|v|1s\epsilon p\rangle - \beta \langle 2pns|v|1s\epsilon p\rangle \right|^2 . \tag{4.87b}$$

This predicts a broad and a narrow series of autoionizing lines converging to the degenerate 2s and 2p configuration of He^+. In the same way, three distinct series of lines should converge to the 3s, 3p, 3d configuration of He^+; each series should maintain a characteristic width.

Such series have been seen in helium, where the discrete-state mixing has been discussed by Fano and Cooper.[45]

d. Static fields

If the atom is influenced by static electric fields, the Hamiltonian H acquires additional terms. These will be included in the operator $\mathcal{V}$. For example, a uniform electric field $\mathbf{\mathcal{E}}$ requires

$$\mathcal{V}' = \sum_i e\,\mathbf{r}_i \cdot \mathbf{\mathcal{E}} \equiv \mathbf{D} \cdot \mathbf{\mathcal{E}} , \tag{4.88}$$

while a point charge e' located at $\mathbf{R}$ requires

$$\mathcal{V}'' = \sum_i \frac{ee'}{|\mathbf{r}_i - \mathbf{R}|} . \tag{4.89}$$

The presence of a strong external field can significantly affect the widths of an excited state which, though above the ionization limit, is prevented from autoionizing by the preceding selection rules. For example, a uniform electric field $\mathbf{\mathcal{E}}$ in the z-direction,

$$\mathcal{V}' = e D_z \mathcal{E}_z \quad , \tag{4.90}$$

can produce autoionizing transitions described by the matrix element

$$\delta(E_I - \omega + E_c) \langle SLJ \| \underset{\sim}{D} \| (S_0 L_0) \epsilon \ell \, S'L'J' \rangle \; \frac{(J'M', 10 \mid JM)}{\sqrt{2J+1}} \; \mathcal{E}_z \quad . \tag{4.91}$$

One then obtains a width having a quadratic dependence on field strength,

$$\Gamma_K^{(elec)}(\epsilon, \mathcal{E}) = \frac{2\pi |\underset{\sim}{\mathcal{E}}|^2}{2J+1} \sum \frac{|\langle SLJ \| \underset{\sim}{D} \| (\bar{S}_0 \bar{L}_0) \epsilon \bar{\ell} \, \bar{S}'\bar{L}'\bar{J}' \rangle|^2}{(2\bar{J}'+1)} \tag{4.92}$$

with the sums again running over barred quantum-numbers at fixed energy ϵ.

It is interesting to note that, although a perturbation $\mathcal{V}'$ may significantly influence the width of an autoionizing line, $\mathcal{V}'$ may have little effect on parameters A_K and B_K. For example, suppose the initial state $|I\rangle$ has even parity and the state $|K\rangle$ has odd parity, so that dipole transitions $\langle I|D_\mu|K\rangle$ are allowed. If $v' = e\underset{\sim}{D} \cdot \underset{\sim}{\mathcal{E}}$, then the autoionizing width receives contributions $|\langle K|\mathcal{V}'|c\rangle|^2$ to even states of the continuum. But the quantity

$$\langle K | v' | c \rangle \langle c | D_\mu | I \rangle \tag{4.93}$$

is zero, since $\langle K|v'|c\rangle \neq 0$ requires an even continuum and $\langle c|D_\mu|I\rangle \neq 0$ requires an odd continuum.

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APPENDIX A: PROFILE PARAMETERIZATION

Other equivalent parameterizations of the function Q(E) of Eq. (1.1) have also been used. Nuclear physicists often use the form[11]

$$Q(E) = \sigma_0(E) + \left| A_{pot} + \frac{A_{res}}{E-E_0+i\,(\Gamma/2)} \right|^2, \tag{A.1}$$

while Fano[44] has suggested

$$Q(E) = \sigma_b(E) + \sigma_a \frac{(\epsilon+q)^2}{\epsilon^2+1}, \tag{A.2}$$

$$\epsilon = (E-E_0)/(\Gamma/2). \tag{A.3}$$

In addition, Fano and Cooper[45] introduced a parameter

$$\rho^2 = \frac{\sigma_a}{\sigma_a+\sigma_b}. \tag{A.4}$$

Another common practice is to parameterize the scattering matrix in the form

$$S_{aa} = \exp(2i\delta) \tag{A.5}$$

with a phase shift

$$\tan(\delta - \delta_0) = \frac{\Gamma/2}{E - E_0} . \tag{A.6}$$

This leads to an attenuation cross-section with the energy dependence

$$Q(E) = -\mathrm{Im}\, T_{aa} = (1 - \cos 2\delta_0) + \frac{\frac{1}{2}\Gamma^2 \cos 2\delta_0 - (E-E_0)\Gamma \sin 2\delta_0}{(E-E_0)^2 + (\Gamma/2)^2} . \tag{A.7}$$

Since all these formulas give identical profiles, a comment on the significance of parameterization (1.1) may be in order.

When parameter A is zero, the profile Q(E) is symmetrical about E_0, Eq. (1.2). With B positive, this profile describes the energy dependence of the photon absorption-coefficients near an ordinary absorption line (in the absence of significant external perturbations to the atoms).

When parameter A is not zero, the profile Q(E) displays a dip on one side of E_0 and a peak on the other side. Physically, this asymmetry arises from coherent interference between direct processes such as potential scattering, which provides a background varying slowly with E, and the formation and decay of a compound state, which varies sharply with E. This interference is sometimes seen in attenuation cross-sections, where the dip in Q(E) appears as a "transmission window" near E_0. Such windows have been noted in the attenuation spectra of s-wave neutrons, shown in Figure 2, and in photon transitions to autoionizing states, shown in Figure 3. Symmetrical windows occur if A = 0 and B is negative.

Empirically, the parameters of Eq. (1.2) have the following significance. The area under the profile is

$$\int Q(E)\,dE = \pi B + \int C(E)\,dE \,. \tag{A.8}$$

If we define a peak height H and a dip depth D (for a Lorentz profile, D = 0) by the relationship

$$H = Q(E_{max}) - C(E_{max}) \tag{A.9}$$

$$D = C(E_{min}) - Q(E_{min}) \tag{A.10}$$

where E_{max} and E_{min} are the energies of maximum and minimum Q(E), then

$$\frac{2B}{\Gamma} = H - D, \qquad \frac{A^2}{\Gamma^2} = HD \tag{A.12}$$

Equations (A.11) permit estimation of profile parameters A and B directly from plots of the profile. In the limiting case A = 0, the width Γ is $E_{max} - E_{min}$, while in the limiting case B = 0, Γ is the full width at the half-maximum of Q(E).

The parameterization of Eq. (1.1) is readily compared with that used by Fano:

$$\sigma = C_k + \frac{(\Gamma_k/2)\,B_k + (E - E_k)\,A_k}{(E - E_k)^2 + (\Gamma_k/2)^2} = \sigma_b + \sigma_a \frac{(\epsilon + q)^2}{\epsilon^2 + 1} \tag{A.12}$$

The parameters are

$$\epsilon = (E - E_k)/(\Gamma_k/2), \tag{A.13a}$$

$$q = -\,\mathrm{Re}\left\{ \frac{t_{qk}^{(a)}}{t_{ak}^{(1)}} \right\}, \tag{A.13b}$$

$$\sigma_a = \frac{2N_a}{\hbar F_a} \frac{| t_{Ka}^{(i)} |^2}{(\Gamma_K/2)}, \tag{A.13c}$$

$$\sigma_b = - \frac{2N_a}{\hbar F_a} \left\{ \mathrm{Im}(t_{aa}) + \frac{| t_{Ka}^{(i)} |^2}{(\Gamma_K/2)} \right\}, \tag{A.13d}$$

$$\rho^2 = \frac{| t_{Ka}^{(i)} |^2}{\mathrm{Im}(t_{aa})\, \mathrm{Im}(t_{KK})}. \tag{A.13e}$$

These relations hold quite generally for the attenuation profile near an isolated resonance; they include the effects of a multichannel continuum and configuration mixing.

It should be noted that each of the formulas for Q(E) involve four parameters, in addition to a background. The present paper uses the real numbers A, B, E_0, Γ, but clearly the parameters q, ρ, E_0, Γ serve as well. For non-autoionizing transitions A vanishes and B and Γ are tied together. (B is essentially the oscillator strength.) Thus, two parameters, E_0 and Γ, suffice to fit ordinary absorption lines.

Footnotes

[1] cf. A. Unsöld, *Physik der Sternatmosphären*, 2nd Ed. (Springer-Verlag, Göttingen, 1955); also Proc. Second Harvard-Smithsonian Conference on Stellar Atmospheres, *The Formation of Spectrum Lines*, Smithsonian Astrophysical Observatory Special Report No. 174, May 1965.

[2] Usually called a Lorentz profile (ref. 3) or, if C = 0, a Breit-Wigner profile: G. Breit and E. P. Wigner, Phys. Rev. 49, 519 (1936).

[3] H. A. Lorentz, *The Theory of Electrons* (Leipzig, 1900; reprinted by Dover Publications, New York, 1952).

[4] This is usually expressed in frequency units: $Q(\omega) = C(\omega) + (\omega - \omega_0)A/[(\omega - \omega_0)^2 + (\Gamma/2)^2]$

[5] cf. G. Breit, "*Dispersion*" in *Encyclopaedic Dictionary of Physics*, ed. J. Thewlis (Pergamon Press, London, 1962)

[6] W. Sellmeier, Pogg. Ann. d. Phys. u. Chem., 143, 271 (1871); 145, 399, 520 (1872); 147, 386, 525 (187)

[7] H. von Helmholtz, Pogg. Ann. d. Phys. u. Chem., 154, 582 (1875)

[8] J. W. Strutt, Phil. Mag. 48, 151 (1899) quotes Maxwell's examination question.

[9] A. G. Shenstone, Phys. Rev. 38, 873 (1931); E. Majorana, Nuovo Cim. 8, 107 (1931); A. G. Shenstone, Repts. Prog. Phys. 5, 210 (1939); W. R. S. Garton, Proc. Phys. Soc. A65, 268. At higher

energies, as initiated by x-ray photons, this decay process is known as an Auger transition: P. Auger, J. Phys. Rad. 6, 205 (1925); cf. E. H. S. Burhop, The Auger Effect and other Radiationless Transitions (Cambridge University Press, 1952).

[10] G. Breit, Phys. Rev. 58, 1068 (1940); cf. ref. 12, Chapter VIII.

[11] J. Blatt and V. Weisskopf, Theoretical Nuclear Physics (John Wiley and Sons, New York, 1952).

[12] P. G. Burke, Advances in Physics 14, 521 (1965).

[13] H. S. W. Massey and D. R. Bates, Rept. Progr. Phys. 9, 67 (1942).

[14] S. G. Kaufman, E. Goldberg, L. J. Koester, and F. P. Mooring, Phys. Rev. 88, 673 (1952).

[15] P. A. M. Dirac, Zeits. f. Phys. 44, 594 (1927); V. Weisskopf and E. P. Wigner, Zeits. F. Phys. 63, 54 (1930); cf. also ref. 17 and ref. 18, chapter V.

[16] G. Breit, Revs. Mod. Phys. 4, 504 (1932).

[17] cf. W. Heitler, Quantum Theory of Radiation, 3rd. Ed. (Oxford Univ. Press, 1954).

[18] cf. M. L. Goldberger and K. M. Watson, Collision Theory (John Wiley and Sons, New York, 1964).

[19] As presented, for example, by refs. 11 and 13-16. This topic is also called collision theory or formal scattering theory. A brief historical resumé of scattering theory with reprints of several papers (in particular, refs. 20 and 26) may be

found in Quantum Scattering Theory, ed. M. Ross (Indiana Univ. Press, Bloomington, Indiana, 1963).

[20] B. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950).

[21] A. Messiah, Quantum Mechanics (John Wiley and Sons, New York, 1962), Chapter XIX.

[22] T. Y. Wu and T. Ohmura, Quantum Theory of Scattering (Prentice Hall, Englewood Cliffs, N. J., 1962).

[23] P. Roman, Advanced Quantum Theory (Addison-Wesley, Reading, Mass. 1965).

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[25] H. Feshbach, Ann. Phys. 5, 357 (1958).

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[27] L. Fonda and R. G. Newton, Ann. Phys. 10, 490 (1960).

[28] J. Humblet and L. Rosenfeld, Nucl. Phys. 26, 529 (1961); L. Rosenfeld, Nucl. Phys. 26, 579 (1961); J. Humblet, Nucl. Phys. 31, 544 (1962); 50, 1 (1964); 57, 386 (1964).

[29] L. S. Rodberg, Phys. Rev. 124, 210 (1961).

[30] M. H. Ross and G. L. Shaw, Ann. Phys. 13, 147 (1961).

[31] H. Feshbach, Ann. Phys. 19, 287 (1962).

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[33] Y. Hahn, T. O'Malley and L. Spruch, Phys. Rev. 134, B911 (1963).

[34] A. Herzenberg, K. L. Kwok, and F. Mandl, Proc. Phys. Soc. 84, 477 (1964).

[35] T. F. O'Malley and S. Geltman, Phys. Rev. 137, A1344 (1965.

[36] P. G. Burke and D. D. McVicar, Proc. Phys. Soc. 86, 989 (1965).

[37] Y. Hahn, Phys. Rev. 139, B212 (1965); 142, 603 (1966).

[38] A. Levin, Phys. Rev. 140, B1099 (1965); 141, 859 (1966); 142, 33 (1966).

[39] L. Lipsky and A. Russek, Phys. Rev. 142, 59 (1966).

[40] W. Miller, Harvard Preprint 1966, to be published.

[41] K. Smith, to be published, 1966.

[42] U. Fano, Phys. Rev. 124, 1866 (1961), an extension of O. K. Rice, J. Chem. Phys. 1, 375 (1933) and U. Fano, Nuovo Cim. 12, 156 (1935).

[43] U. Fano and F. Prats, J. Nat. Acad. Sci. India, to be published.

[44] F. Prats and U. Fano, in Atomic Collision Processes, edited by M. R. C. McDowell (North-Holland Publishing Co., Amsterdam, 1964), p.600.

[45] U. Fano and J. W. Cooper, Phys. Rev. 137, A1364 (1965).

[46] Ref. 34 has considered the connection between the S matrix, the K matrix, and diagonalization procedure.

[47] For recent reviews of "pressure broadening," consult H. Griem, Plasma Spectroscopy (McGraw-Hill, New York, 1965); H. van Regemorter, Ann. Rev. Astron. and Astrophys. 3, 71 (1964); M. Baranger, in Atomic and Molecular Processes, ed. D. R. Bates (Academic Press, New York, 1962).

[48] The symbol S_a denotes summation over discrete indices (say m,n...) and integration over continuous indices (say x,y...) including energy, E_a if that is a continuous variable: $S_a = \sum_n \sum_m \cdots \int dx \int dy \cdots \int dE_a$. For convenience, I assume delta-function normalization for continuum functions; another choice of normalization would introduce a factor ρ_a, the density of states, into the definition of S_a.

[49] J. A. Wheeler, Phys. Rev. 52, 1107 (1937); W. Heisenberg, Zeits. f. Phys. 120, 513 and 673 (1943).

[50] The superscript $^+$ distinguishes the outgoing-wave solutions Ψ^+ from incoming-wave Ψ^- or standing-wave Ψ^1 solutions.

[51] P. A. M. Dirac, The Principles of Quantum Mechanics, 4th ed. (Oxford Univ. Press, 1958).

[52] Alternative prescriptions for the singularity at $E_a = E_b$ give incoming scattered waves and standing scattered waves; cf. ref. 20. The standing-wave equation is $\Psi_a^1 = \psi_a + S'_a \psi_b \langle \psi_b | V | \Psi_a^+ \rangle / (E_a - E_b)$.

[53] C. C. Grosjean, Formal Theory of Scattering Phenomena. Institut Interuniversitair des Sciences Nucleaires Monographie No. 7 (Brusselles, 1960), p.29.

[54] Although $G^o(E)$, $G(E)$, and $\mathcal{T}(E)$ are functions of $E \equiv E_a$, this dependence will not always be shown; I shall write simply G^o, G, and $\mathcal{T}$. The limit $\eta \to 0^+$ should be understood.

[55] A few authors denote this operator by the letter R; others define T without the factor of $2\pi i$ in Eq. (2.23).

[56] The present discussion deals with a stationary target; momentum is not conserved in such collisions. A refined treatment of collisions between light particles gives a factor $\delta(\underset{\sim}{p}_a - \underset{\sim}{p}_b)$ insuring conservation of momentum; cf. ref. 18.

[57] cf. ref. 11, p.317.

[58] When Eq. (2.31) is integrated over final-state energy dE_b, it takes the familiar form $\sigma(a \rightarrow b) = (2\pi/\hbar)(\rho_a/F_a)\ |T_{ab}|^2$ where ρ_a is the density of states. (With the present normalization, $\rho_a = 1$).

[59] R. W. Ditchburn, Light, 2nd Ed. (Interscience Publishers, New York, 1963).

[60] M. Garbuny, Optical Physics (Academic Press, New York, 1965).

[61] Previous authors have given this result in the form $\underset{\sim}{\tilde{n}}_a - 1 = 2\pi N_a f_{aa}(0)/k_a^2$ where $f_{aa}(0)$ is the forward scattering amplitude; cf. E. Fermi, Nuclear Physics, p.201 (Univ. of Chicago Press, 1950); J. M. Jauch and F. Rohrlich, The Theory of Photons and Electrons, Appendix A7 (Addison-Wesley, Reading, Mass. 1955); S. de Benedetti, Nuclear Interactions (John Wiley and Sons, New York, 1963), Section 3.19; ref. 21, p.867.

[62] N. Bohr, R. Peierls, and G. Placzek, Nature 144, 200 (1939). The theorem was earlier proven for elastic scattering by E. Feenberg, Phys. Rev. 40, 40 (1932).

[63] Such a connection was noted by Maxwell, ref. 8, and von Helmholtz, ref. 7.

[64] R. de L. Kronig, J. Opt. Soc. Am. 12, 547 (1926); H. A. Kramers, *Estratto dagli Atti de Congresso Internazionale de Fisici Como* (Bologna, 1927). cf. ref. 59, p.772.

[65] cf. ref. 50, Chapter XV.

[66] A. J. F. Siegert, Phys. Rev. 56, 750 (1939).

[67] M. G. Mittag-Leffler, Acta Soc. Scient. Fennicae XI, 273 (1880); cf. E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th Ed. (Cambridge Univ. Press, 1927).

[68] Lengthy discussions may be found in Refs 18 and 23 and in R. G. Newton, J. Math. Phys. 1, 319 (1960).

[69] Ref. 11, Chapter X.

[70] A. M. Lane and R. G. Thomas, Rev. Mod. Phys. 30, 257 (1958).

[71] G. Breit, Handb. d. Phys. XLI/1, 1 (Springer-Verlag, Berlin, 1959).

[72] Projection operators have been used in similar context by refs. 21, 26, 27, 29, 31, 73 and numerous more recent papers.

[73] H. Feshbach, Ann. Rev. Nucl. Sci. 8, 49 (1958).

[74] Ref. 21, p.995.

[75] E.g. L. Mower, Phys. Rev. 142, 799 (1966).

[76] G_P and t depend on incident energy E and on the choice of the partition of states into P and Q.

[77] Rodberg, ref. 29, has given a similar equation but with single-particle operators in place of the present many-particle , V, and .

[78] This approach was suggested in ref. 31.

[79] These two parts will be determined in Section III. In principle, one can let $t_{bK}^{(r)} = \frac{1}{2}(t_{bK} + t_{Kb})$ and $t_{bK}^{(i)} = -\frac{i}{2}(t_{bK} - t_{Kb})$.

[80] E.g. F. B. Hildebrand, *Methods of Applied Mathematics*, 2nd Ed., p.16 (Prentice Hall, Englewood Cliffs, New Jersey, 1965).

[81] E.g., ref. 21, Chapter XVI.

[82] Single-mode photon operators may also be included, as will be discussed in the following.

[83] For example $|a\rangle$ might be a determinantal function for fermions.

[84] The remainder of this paragraph applies only to states for particles with non-zero mass, not to photons. However, photons may still be treated as projectiles, as the following discussion will show.

[85] V. Fock, Zeits. f. Phys. 75, 622 (1932). cf. S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory*, Chapter 6 (Harper and Row, 1961).

[86] E. A. Power, *Introductory Quantum Electrodynamics* (Longmans, London, 1964).

[87] This diagonalization excludes continuum states: they are not components of the resonance state defined in the present paper.

[88] E.g. in the Z-expansion formalism of Layzer, ref. 89, configurations having the same parity and principal quantum number are treated as degenerate.

[89] D. Layzer, Ann. Phys. 8, 271 (1959).

[90] I assume that $\langle a|V|a \rangle$ is real.

[91] Following the pictorial approach of R. P. Feynman, Phys. Rev. 76, 749, 769 (1949) and Theory of Fundamental Processes, (W. A. Benjamin, New York, 1961).

[92] In the form $2\pi\ \rho(E_c)\ |\langle c|V|K \rangle|^2$ with ρ the density of states, this will be recognized as Fermi's Famous Golden Rule for transition probabilities (Fermi, ref. 61, p.142).

[93] Note that this sum includes elastic scattering, in which the projectile changes only direction. In particular it includes the term $|\langle a|V|a \rangle|^2$ which describes elastic scattering in the forward direction.

[94] As with parameter C, the summation includes elastic scattering.

[95] This argument was used by Blatt and Weisskopf, ref. 11, p.469 based on Eq. (2.43). The present paper simply points out how Eq. (2.42) offers the same conclusion.

[96] R. E. Peterson, H. H. Barschall and C. K. Bockelman, Phys. Rev. 79, 593 (1950).

[97] Many standard texts discuss this problem, e.g. H. A. Kramers, Quantum Mechanics, Chapter VIII (North-Holland Publishing Co., 1957; reprinted by Dover Publications, New York, 1964) or ref. 21,

Chapter XXI. More complete discussions will be found in refs. 17, 98, and 99. D. A. Tidman, Nucl. Phys. 2, 289 (1956) and C. A. Mead, Phys. Rev. 110, 359 (1958), 112, 1843 (1958), 120, 854 (1960), 128, 1783 (1962) have examined the quantum theories of the refractive index.

[98] A. I. Akhiezer and V. B. Berestetskii, Quantum Electrodynamics (Interscience Publishers, New York, 1965).

[99] N. M. Kroll, in Quantum Optics and Electronics, edited by C. de Witt and A. Blandin (Gordon and Breach, New York, 1965).

[100] Cf. ref. 98, Section 38 or T. Itoh, Revs. Mod. Phys. 37, 159.

[101] This choice for V_{rad} rather than the more common expression $e\mathbf{p}\cdot\mathbf{A}/mc + e^2A^2/2mc^2$ is discussed by Power, ref. 86; cf. M. Goeppert-Mayer, Ann. Phys. 9, 273 (1931); J. Fuitak, Can. J. Phys. 41, 12 (1962); N. Bloembergen in Quantum Optics and Electronics, edited by C. de Witt and A. Blandin (Gordon and Breach, New York, 1965).

[102] The flux F_a is now N_γ times the flux in $|I,1_\gamma\rangle$.

[103] Conventional treatments of radiation, such as references 17, 21, 86, and 98, derive this result with the aid of photon creation and annihilation operators.

[104] G. Mie, Ann. Phys. 25, 377 (1908); H. C. Corben and J. Schwinger, Phys. Rev. 58, 953 (1940).

[105] T. L. Hill, Am. J. Phys. 22, 211 (1954).

[106] M. E. Rose, Multipole Fields (John Wiley and Sons, New York, 1955); M. E. Rose, Elementary Theory of Angular Momentum (John Wiley and Sons, New York, 1957), Chapter VII.

[107] cf. A. Edmonds, Angular Momentum in Quantum Mechanics (Princeton, 1957).

[108] Ref. 11, Appendix B.

[109] K. Gottfried, Quantum Theory (Benjamin, New York, 1966).

[110] To include higher multipoles consistently, one must include a term $\sum_i \underset{\sim}{\mu}_i \cdot \underset{\approx}{\mathcal{H}}(i)$ in the Hamiltonian where $\underset{\sim}{\mu}_i$ is the magnetic moment of the ith electron.

[111] Lengths are measured in units of $a_0 = 5.29167 \times 10^{-9}$ cm; energies in units of 27.21070 eV, twice the ionization energy of hydrogen; time is measured in units of $a_0/\alpha c = 2.419 \times 10^{-17}$ sec

[112] cf. ref. 86, Chapter 9.

[113] cf. E. U. Condon and G. H. Shortly, The Theory of Atomic Structure (Cambridge Univ. Press, 1935), Chapters VII-VIII.

[114] cf. A. de Shalit and I. Talmi, Nuclear Shell Theory (Interscience Publishers, New York, 1963).

[115] B. W. Shore, Phys. Rev. 139, A1042 (1965).

[116] G. Racah, Phys. Rev. 63, 367 (1943).

[117] cf. ref. 103, p.118.

[118] These states are presumed to be properly antisymmetrized, hence my reference to an added orbital rather than an added electron.

[119] R. D. Cowan and K. L. Andrew, J. Opt. Soc. Am. 55, 502 (1965).

[120] I. B. Levinson and A. A. Nikitin, Handbook for Theoretical Computation of Line Intensities in Atomic Spectra (translation published by Daniel Davies, New York, 1965).

[121] G. Racah, Phys. Rev. 61, 537 (1942); G. Racah, J. Opt. Soc. Am. 50, 408 (1960).

[122] The S-Matrix theory of natural line-widths has been given by F. Low, Phys. Rev. 88, 53 (1952).

[123] cf. ref. 21, p.998.

[124] R. Ladenburg, Z. Phys. 34, 408 (1925); cf. R. W. Nicholls and A. L. Stewart in Atomic and Molecular Processes, edited by D. R. Bates (Academic Press, New York, 1962), Chapter 2 or L. H. Aller, Astrophysics. The Atmospheres of the Sun and Stars, 2nd Ed. (The Ronald Press Co., New York, 1963), p.296. Condon and Shortley, ref. 113, p.108, denote my f_{IK} as f_{KI}; however, the present notation has become more common.

[125] The emission oscillator-strengths f_{Kn} and df_{Kc}/dE_c are negative, so γ_K is positive.

[126] The classical radiation-damping constant (M. Planck, Ann. Phys. 60, 577, 1899) is $8\pi^2\alpha/3\lambda_0^2$ in present units.

[127] H. E. White, Phys. Rev. 38, 2016 (1931); A. G. Shenstone, Repts. Prog. Phys. 5, 210 (1939); cf. also ref. 113, Section 3.15.

[128] F. Paschen, Sitz. Preuss. Akad. Wiss. 32, 709 (1931).

[129] cf. ref. 51, p.248 or ref. 16.

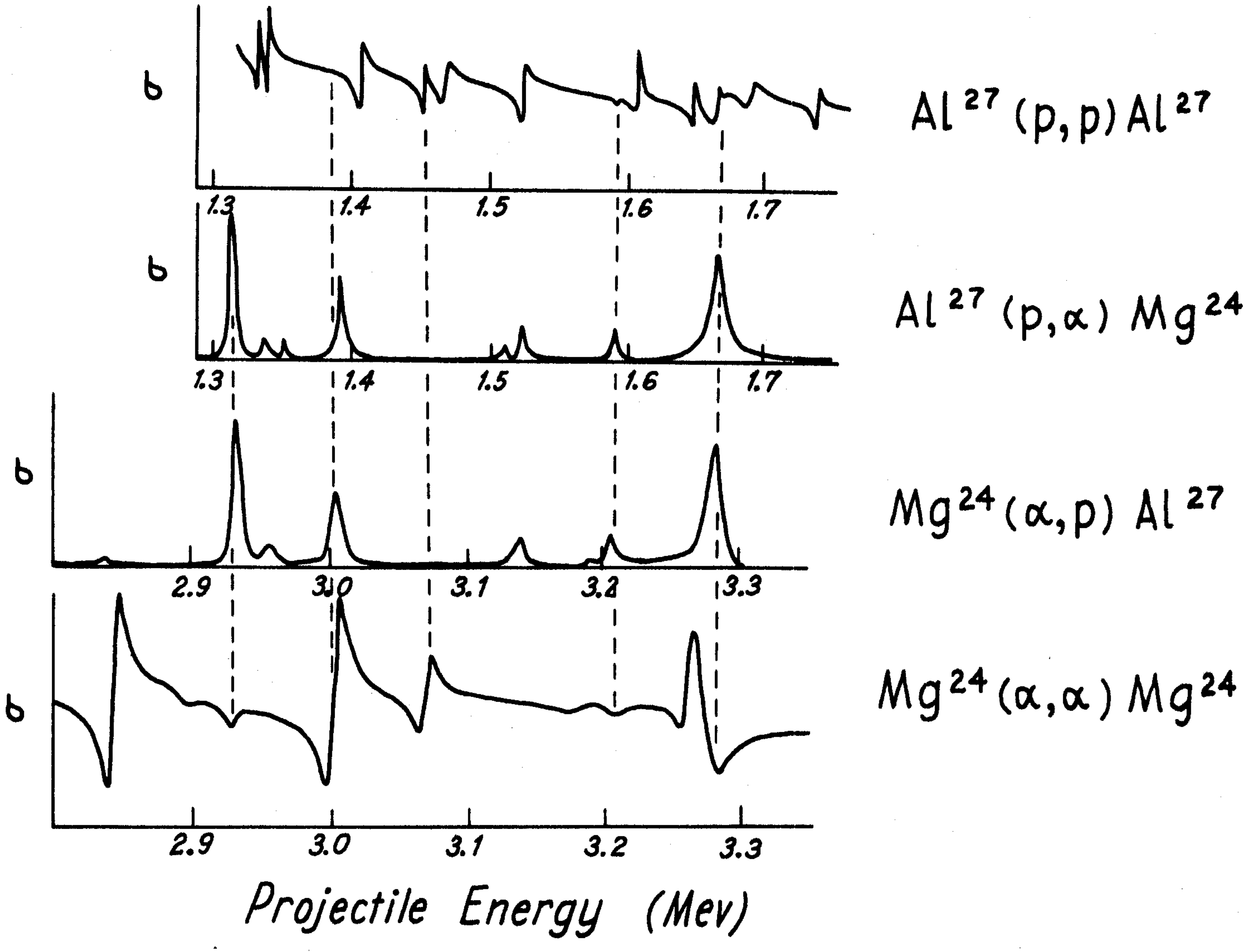
[130] H. E. Moses, in a Lincoln Laboratory Preprint, 4 February 1966, has remarked on this formula.

[131] J. W. Strutt, Phil. Mag. XLI, 107 (1871).

Caption

FIG. 1. Relative cross-sections for reactions leading to compound states of Si^{28}. Projectile energy in center-of-mass system, cross-sections in arbitrary units. (Data of S. G. Kaufman, E. Goldberg, L. J. Koester, and F. P. Mooring, Phys. Rev. 88, 673, 1952).

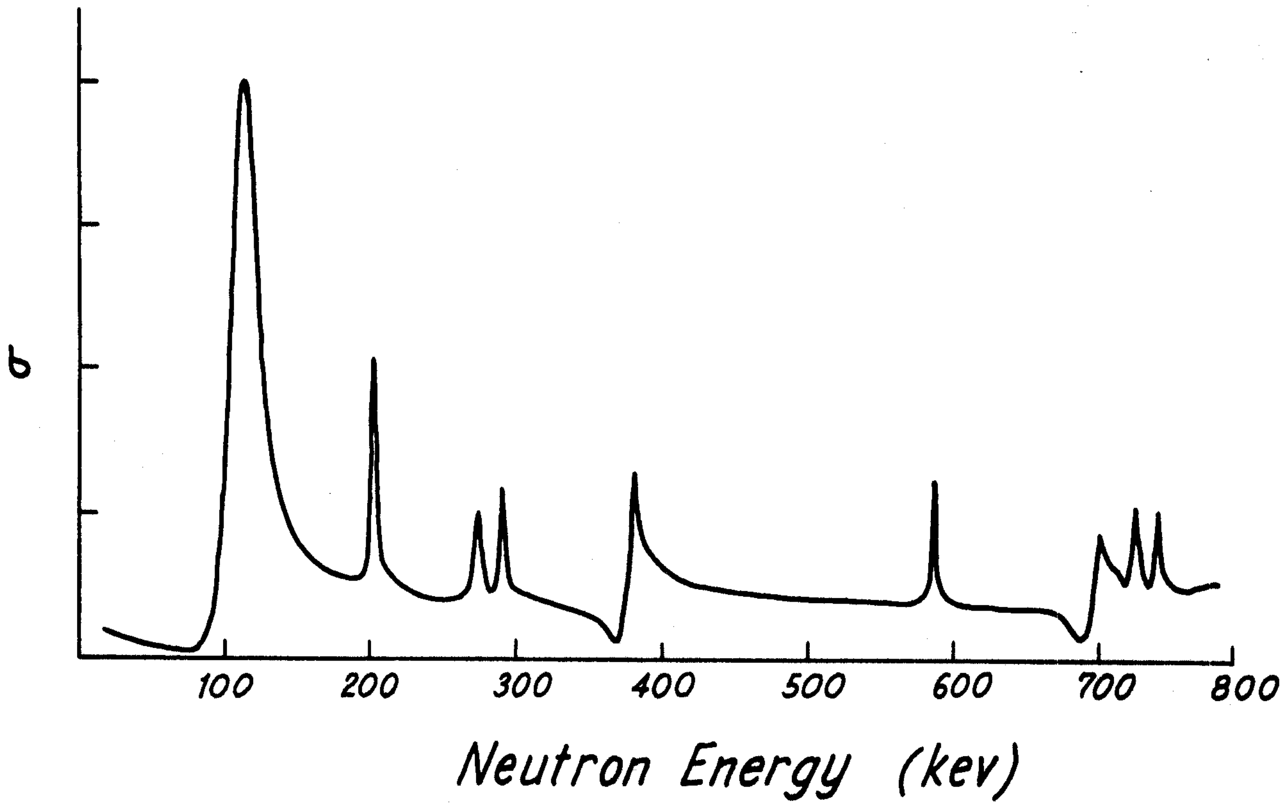
FIG. 1


$Al^{27}(p,p)Al^{27}$
$Al^{27}(p,\alpha)Mg^{24}$
$Mg^{24}(\alpha,p)Al^{27}$
$Mg^{24}(\alpha,\alpha)Mg^{24}$
σ
σ
σ
σ
1.3
1.4
1.5
1.6
1.7
1.3
1.4
1.5
1.6
1.7
2.9
3.0
3.1
3.2
3.3
2.9
3.0
3.1
3.2
3.3
Projectile Energy (Mev)

Caption

FIG. 2. Total neutron attenuation cross-section for sulfur. (From R. E. Peterson, H. H. Barschall, and C. K. Bockelman, Phys. Rev. 79, 593, 1950).

FIG.2



Caption

FIG. 3. Photon attenuation cross-section for neutral barium. Cross-section in arbitrary units. (Data from W. R. S. Garton, Harvard C ollege Observatory Shock-Tube Spectroscopy Laboratory Scientific Report No. 6, November, 1965).

FIG. 3