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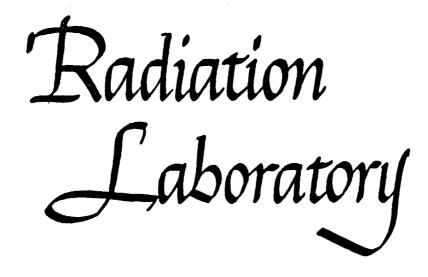**Authors**
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ABSTRACT

A new technique is described for calculation of the scattering of charged particles by atoms. This is done by means of an expansion in "incoherent fluctuations" of the state of the atom. Two limiting cases are discussed - the adiabatic and the high-energy limits. The structure and convergence of the expansion are investigated. Several variational techniques may be used within the framework of the method described. Finally, a detailed study is made of scattering by hydrogen atoms.

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I. INTRODUCTION

We should like to discuss a novel technique for describing the scattering of charged particles by atoms. The method may be readily generalized to describe the scattering of one complex system by another (for example, the scattering of molecules by molecules); we shall, however, limit our scope to the following problem.

A simple particle (without internal degrees of freedom, except possibly angular momentum) of charge Q is scattered by a single neutral atom, having atomic number Z. Our problem is to determine the scattering cross section. To provide a first simple presentation, we shall either suppose that the incident particle is not an electron, or, if it is an electron, we shall suppose that its exchange interactions with the orbital electrons of the atom are negligible. In Part II, we shall show that a simple modification of our method suffices to include exchange effects because of the Pauli principle.

The formulation to be presented provides in principle an exact solution to the problem. Thus approximation methods may be studied systematically. We shall also show that our technique lends itself to several variational methods, providing means for practical computation.

The bulk of our discussion, after the presentation of the method, will be concerned with the physical basis of several methods of approximation and the resulting rapidity of convergence. In the course of doing this, we shall show how other techniques for such problems are related to that given here.

The Hartree-Fock method provides one of the most elaborate devices that has been used in handling atomic-scattering problems.[1] This is, indeed, somewhat related to our method. In contrast to the method presented here, however, the Hartree-Fock formulation does not lend itself to systematic improvement to arbitrary accuracy. Buckingham has used another variational method to obtain a polarization potential.[2,3] This appears in a definite approximation (the adiabatic approximation) in our discussion, where a novel variational technique is employed to obtain it. Nonadiabatic corrections to the polarization potential are also formulated from a variational principle. It will not be assumed that the interactions responsible for the scattering are weak. Instead, an expansion will be made in the number and complexity of the "discontinuous changes in orbit" that the scattered particle makes. More precisely, by a "discontinuous change of orbit" we mean a single scattering interaction that leads to a change in the state of the atom. Such an <u>inelastic scattering</u> changes the wave number of the scattered particle, so that the resulting scattered wave does not interfere with the unscattered wave. Using the concept of scattered waves, we may re-express our method as providing an expansion in "incoherent" scattering processes.

The expansion just described appears to have rather simple features in several limiting cases. For scattering of fast particles, the method converges rapidly, partly because the interactions are effectively weaker at high energies and partly because the incoherent scatterings are more readily "localized" in space. For slow massive particles, or for slow particles scattered by atoms of large atomic number, our method gives immediately the classical limit of a particle moving in a potential well.

To actually determine the scattering, one must first compute the "potential well" in which the scattered particle travels within the atom. Inelastic scatterings of the particle with individual electrons are treated as if occurring <u>impulsively</u>; however, between such impulsive interactions the particle travels "smoothly" in its potential well.

This type of treatment has been used for a variety of phenomena in nuclear physics. These include stripping and pickup processes,[4,5] as well as elastic scattering and transport phenomena.[6] The specific method that is given here is a modified form of that used to describe high-energy nuclear interactions.[7,8] The applicability of these techniques to low-energy nuclear interactions has been demonstrated by Brueckner and his collaborators.[9,10]

For these latter applications, it was important to assume that an atomic nucleus has many of the properties of a nearly degenerate Fermi gas - a condition that is also found in the electronic structure of all but the lightest atoms. Because electromagnetic interactions are weaker and of longer range than nuclear forces, we shall actually find that our problem is simpler than the corresponding ones in nuclear physics.

In the next section, the formulation of the technique just described is presented. We shall see how to apply it to either elastic or inelastic scattering of a charged particle by an atom. In the following section, we shall obtain both the adiabatic and high-energy approximations and discuss the conditions for their applicability. In Section IV a more detailed investigation of the adiabatic limit will be given based on the Fermi-Thomas model. In Section V, the scattering by hydrogen atoms will be discussed. Finally, in Section VI, the applicability of several variational principles will be demonstrated.

II. FORMAL DEVELOPMENT

It is assumed that the neutral atom is described by a Hamiltonian H_A, a set of energy eigenvalues W_n ($n = 0, 1, 2 \ldots$), and a complete set of wave functions ϕ_n. The ground-state energy and wave function are denoted respectively, by W_0 and ϕ_0.[11] Thus, we have

$$H_A \phi_n = W_n \phi_n. \tag{2-1}$$

The coordinates of the electron are represented by $Z_\ell (\ell = 1, 2 \ldots Z)$, and the mass of an electron by m. The particle to be scattered has a mass M_0 and a charge Q.

The scattering is considered in the center-of-mass coordinate system. The initial kinetic energy is ϵ_0. The kinetic energy in general is

$$K(p) = \frac{p^2}{2M} \, ,$$

where p is the relative momentum of particle and atom, and M is their reduced mass.[12] The interaction energy of the particle with the atom is written as

$$V_N + V,$$

where

$$V_N = \frac{ZeQ}{X} \qquad (2-2)$$

and

$$V = \sum_{\ell=1}^{Z} V_\ell \ ,$$

with

$$V_\ell = \frac{e'Q}{|\underset{\sim}{X} - \underset{\sim}{Z}_\ell|} \ . \qquad (2-3)$$

Here $e' = -e$ is the charge on an electron and $\underset{\sim}{X}$ is the coordinate of the scattered particle, measured with respect to the atomic nucleus (which we consider as at a point) .

The scattering of the particle by the atom is now described by the Schrödinger equation

$$[K + V_N + V + H_A]\ \Psi = [\epsilon_0 + w_0]\ \Psi. \qquad (2-4)$$

This is more conveniently written as an integral equation.[13]

$$\Psi = \chi_0 + \frac{1}{a}\ (V + V_N)\ \Psi\ ,$$

where

$$\chi_0 = \frac{e^{i\underset{\sim}{p}_0 \cdot \underset{\sim}{X}}}{(2\pi)^{3/2}}\ \phi_0, \qquad (2-5)$$

and

$$a \equiv \epsilon_0 - K + i\eta + (W_0 - H_A). \qquad (2-6)$$

(Here η is a positive infinitesimal parameter that determines the contour of integration past the pole of a^{-1}.) The incident wave is χ_0 in Eq. 2-5.

The wave function Ψ may conveniently be expanded in terms of ϕ_n:

$$\Psi = \sum_n \psi(\underset{\sim}{X}, n)\ \phi_n. \qquad (2-7)$$

The elastic scattering is given by the term with $n = 0$:

$$\Psi_c \equiv \psi(\underset{\sim}{X}; 0)\ \phi_0. \qquad (2-8)$$

To condense our notation, we write (2-7) as

$$\Psi = F \Psi_c,$$ (2-9)

where $(\phi_o, F \phi_0) = 1$ and $(F-1)$ has matrix elements for inelastic scattering only.

As we shall see, the elastic scattering may be obtained from an equivalent potential $\mathcal{V}$, such that

$$[K + \mathcal{V}] \psi (\underset{\sim}{X}, 0) = \epsilon_o \psi (\underset{\sim}{X}, 0).$$ (2-10)

The potential $\mathcal{V}$ depends only upon the coordinate $\underset{\sim}{X}$ of the scattered particle, so Eq. (2-10) actually describes the motion of a single particle in a fixed-force field. We shall always consider Eq. (2-10) as a soluble problem, that is, one for which we need not find approximations.

It is desirable to generalize $\mathcal{V}$ to a potential $\mathcal{V}$(n) which describes the elastic scattering of the particle in an excited state n, although for many applications one may suppose that $\mathcal{V}$(n) does not depend very strongly on n. However, it is very important that the matrix $\mathcal{V}$ is diagonal in the state n of the atom .[14]

The potential $\mathcal{V}$ will be explicitly determined later; for the moment, however, let us suppose it to be known. Then Eq. (2-10) may be rewritten as

$$\Psi_c = \chi_o + \frac{1}{a} \mathcal{V} \Psi_c.$$ (2-11)

Because $\mathcal{V}$ is diagonal in the atomic states, a is just $(\epsilon_o - K + i\eta)$ in Eq. (2-11).

Now, in order that Eqs. (2-9) and (2-11) be consistent with (2-5), we find that F must satisfy the matrix equation

$$F = 1 + \frac{1}{d} [V_N + V - \mathcal{V}]F,$$

with

$$d \equiv a - \mathcal{V}.$$ (2-12)

To see this, we substitute Eqs. (2-11), (2-12), and (2-9) into the right-hand side of (2-5) to obtain

$$\Psi = \chi_o + \frac{1}{a} (V + V_N) F \Psi_c.$$

Now

$$\frac{1}{a} = \frac{1}{d} + \frac{1}{a}(d-a)\frac{1}{d} = \frac{1}{d} - \frac{1}{a}\,\mathcal{V}\frac{1}{d} \tag{2-13}$$

is a simple algebraic identity, which permits us to write

$$\frac{1}{a}(V + V_N)F = [1 - \frac{1}{a}\,\mathcal{V}]\frac{1}{d}[V + V_N - \mathcal{V} + \mathcal{V}]F$$

$$= [1 - \frac{1}{a}\,\mathcal{V}][F - 1 + \frac{1}{d}\,\mathcal{V}F],$$

using the Eq. (2-12) satisfied by F. Now we have

$$\Psi = \chi_0 + [1 - \frac{1}{a}\,\mathcal{V}][F - 1 + \frac{1}{d}\,\mathcal{V}F]\,\Psi_c$$

$$= [\chi_0 + \frac{1}{a}\,\mathcal{V}\Psi_c] - \Psi_c + F\,\Psi_c + [-\frac{1}{a} + \frac{1}{d} - \frac{1}{a}\mathcal{V}\frac{1}{d}]\mathcal{V}F\,\Psi_c.$$

The first two terms cancel because of Eq. (2-11). The last term vanishes because of Eq. (2-13). The remaining term is $F\,\Psi_c$, which verifies that Eq. (2-9) provides a solution to Eq. (2-5).

Thus far, all that we have said is formally exact - but not useful, because we have not yet determined the potential $\mathcal{V}$. To obtain $\mathcal{V}$, we use the condition that (F-1) must describe only inelastic scatterings. That is, we require that F satisfy the equation

$$F = 1 + \frac{1}{d}\,P[V_N + V]\,F. \tag{2-14}$$

Here P is an operator that instructs us never to repeat a given state "n" of the atom in the perturbation expansion for F:[8]

$$F = 1 + \frac{1}{d}P(V_N + V) + \frac{1}{d}P(V_N + V)\frac{1}{d}P(V_N + V) + \ldots .$$

The general term is

$$\sum_{n_2, n_3 \ldots n_s} (n_1|\frac{1}{d}P(V_N + V)|n_2)(n_2|\frac{1}{d}P(V_N + V)|n_3)\ldots(n_s|\frac{1}{d}P(V_N + V)|0).$$

The operators P instruct us that the atomic states n_1, n_2, $\ldots n_s$, 0 must all be different. Aside from this restriction on states, P has no other effect on the perturbation series. In particular, it does not act on the states of the scattered particle.

We may finally determine $\mathcal{V}$ from the condition that Eqs. (2-14) and (2-12) be equivalent. Indeed, we may rewrite Eq. (2-12) as

$$F = 1 + \frac{1}{d} P(V_N + V) F + \frac{1}{d}[(1-P)(V_N+V) - \mathcal{V}] F.$$

For (2-12) and 2-14) to be equivalent in general, we must obviously have

$$\left\langle n|\mathcal{V}F|0\right\rangle = \left\langle n|(1-P)(V_N+V)F|0\right\rangle .$$

Because we require that $\mathcal{V}$ be diagonal in the states n, this may be written as

$$\left\langle n|\mathcal{V}|n\right\rangle \left\langle n|F|0\right\rangle = \left\langle n|(1-P)(V_N+V)F|0\right\rangle . \tag{2-15}$$

Now (1-P) is an instruction that tells us that the state "n" must have occurred someplace in the perturbation expansion for F. It may have occurred at the previous interaction, at the second previous interaction, etc. This may be expressed as[8]

$$\left\langle n|(1-P)(V_N+V)F|0\right\rangle = \left\langle n|(V_N+V)|n\right\rangle \left\langle n|1+\frac{1}{d}P(V_N+V) + \ldots |0\right\rangle$$

$$+ \left\langle n|(V_N+V)\frac{1}{d}P(V_N+V)|n\right\rangle \left\langle n|1+\frac{1}{d}P(V_N+V)+\ldots |0\right\rangle$$

$$+ \ldots$$

$$= \{\left\langle n|[(V_N+V)+(V_N+V)\frac{1}{d}P(V_N+V)+\ldots]|n\right\rangle\}\left\langle n|F|0\right\rangle$$

$$= \left\langle n|(V_N+V)F|n\right\rangle \left\langle n|F|0\right\rangle . \tag{2-16}$$

On comparing this with Eq. (2-15), we see that

$$\mathcal{V}(n) \equiv \left\langle n|\mathcal{V}|n\right\rangle = \left\langle n|(V+V_N)F|n\right\rangle \tag{2-17}$$

defines the potential $\mathcal{V}$. Finally, we may (for most practical purposes) drop the V_N in Eq. (2-14) for F. That is, the operator P in F implies that each matrix element of $(V_N + V)$ changes the state of the atom. Except for very energetic nuclear interactions (which we are not considering) the electrons can follow adiabatically the recoil of the nucleus associated with V_N, so we have[15]

$$P V_N \simeq 0. \tag{2-18}$$

We may now summarize our scattering equations:

$$\Psi = F \Psi_c$$

$$\Psi_c = \chi + \frac{1}{a} \mathcal{V} \Psi_c$$

$$F = 1 + \frac{1}{d} PVF$$

$$d \equiv \epsilon_o + i\eta - \epsilon + (W_o - W_n)$$

$$\mathcal{V}(n) = V_N + \langle n | VF | n \rangle$$

$$\epsilon = K + \mathcal{V}. \tag{2-19}$$

The fact that V_N, which is in general the strongest interaction term, occurs only in one place (and in a trivial manner) in our equation (2-19) simplifies subsequent applications considerably. Indeed, this point has frequently arisen before in atomic-scattering problems and has on occasion caused difficulties.

As described in the Introduction, the separation of "coherent" and "incoherent" interactions has now been achieved. Indeed, the physical interpretation of the wave function Ψ in the form (2-19) is that the particle moves "smoothly" as determined by the potential $\mathcal{V}$ between inelastic interactions, these being determined by (P V) in F.

When the scattered particle has a positive charge, it may pick up one or more electrons before the scattering is complete. "Such rearrangement collisions" are of course included in our wave function Ψ. Some care in application is called for because in such collisions one must expand the outgoing wave in terms of eigenfunctions of the two outgoing systems. This means expanding the last $\frac{1}{d}$ in F in terms of the appropriate new Green's function. When this is done, one obtains the appropriate starting point for a discussion of the "pick-up" cross section. In Part II we shall return to a detailed discussion of this type of process. We note for later reference, however, that a first approximation would give the familiar result

$$R = 2\pi \int \delta(\epsilon_o + W_o - E_f) |(X_f, V \Psi_c)|^2 d_\tau \tag{2-20}$$

for the "rearrangement" transition rate. Here X_f is the final wave function, describing the 2-product atomic systems and E_f is their appropriate energy. The volume element of integration over final status is written as "$d\tau$". Finally, the cross-section for the rearrangement collision is

$$\sigma = \frac{(2\pi)^3}{V} R, \qquad (2-21)$$

where V is the initial relative velocity of the incident particle and the original atom, and $(2\pi)^{-3}$ is the incident-particle flux with our normalization.

III. APPROXIMATE FORMS FOR $\mathcal{V}$

When the potentials $\mathcal{V}$ and V are approximately constant over a distance of the order of one wavelength of the scattered particle, we may expect to approximate d in the equation for F by a much simpler quantity. In this case, the scattered particle undergoes a very large number of scatterings, each giving it a very small impulse. If this condition obtains, the kinetic energy of the scattered particle will not change appreciably when a scattering occurs, so the kinetic-energy operator may be neglected in the denominators d that occur in F.

To express this in detail, we note that for a particle moving in a potential well, the condition of energy conservation is

$$\epsilon_0 = K + \mathcal{V}(0).$$

When rapid fluctuations in the atomic state occur, but under conditions such that the kinetic energy of the scattered particle is not modified, the virtual energy of the particle is

$$\epsilon = K + \mathcal{V}(n).$$

The energy difference $[\epsilon_0 - \epsilon]$ in d is then $[\mathcal{V}(0) - \mathcal{V}(n)]$ which is just the difference between the two expressions above.

In this case we have the so-called adiabatic approximation. The denominators d occurring in F are replaced by

$$d \simeq d_A \equiv [\mathcal{V}(0) - \mathcal{V}(n)] + (W_0 - W_n). \qquad (3-1a)$$

For a degenerate Fermi gas the excitations $(W_o - W_n)$ tend to be large; thus it appears that the difference $[\mathcal{V}(0) - \mathcal{V}(n)]$ above will often be negligible in d_A. For many practical applications the simpler equation

$$d \approx d_A = W_o - W_n \tag{3-1b}$$

seems quite adequate. This may be seen most easily in terms of the Hartree-Fock model. The potentials $\mathcal{V}(n)$ depend upon averages over all electrons. Thus, when only a few electrons at a time are excited, $\mathcal{V}(n)$ may differ but little from $\mathcal{V}(0)$. For our subsequent discussions of the adiabatic approximation, we shall often assume (3-1b).

As an example, in the limit when classical mechanics is valid, the particle scatters continuously, each scattering corresponding to an infinitesimal momentum transfer. For such interactions, the difference $[\epsilon - \epsilon_o]$ is vanishingly small.

When either Eq. (3-1a) or Eq. (3-1b) is valid, the coordinate $\underset{\sim}{x}$ of the scattered particle commutes with d_A and thus with F. It appears therefore only as a parameter in the equations for F and $\mathcal{V}$, so

$$\mathcal{V}(\underset{\sim}{x}) = \frac{ZeQ}{x} + \left\langle n | V(x) F(x) | n \right\rangle \quad . \tag{3-2}$$

This potential describes the interaction energy of a charge Q at a distance x from the nucleus. (We shall compare this result with the more conventional ones in Sec. VI.) Expanding F, we have

$$\mathcal{V}(x) = \frac{ZeQ}{x} + \left\langle n | V(x) | n \right\rangle + \left\langle n | V(x) \frac{1}{d_A} P V(x) | n \right\rangle + \ldots \quad . \tag{3-3}$$

The first two terms represent the potential of the nucleus as shielded by the orbital electrons - a familiar result. The higher order terms represent corrections to this because of the polarization of the atom by the extra particle.

We may express this in more conventional terms. If the charge density of electrons in the atom is $\rho(Z)$, we may write this as

$$\rho(Z) = \rho_o(Z) + \delta\rho(Z) \tag{3-4}$$

Here $\rho_o(Z)$ is the charge density of the original atom before it was perturbed by the charge Q and $\delta\rho$ is the change in ρ due to the perturbing effect of Q.

The energy of interaction of Q, when at $\underset{\sim}{x}$, with the atom is

$$\Delta E = \frac{ZeQ}{x} + Q \int \frac{\rho_o(Z)d^3Z}{|\underset{\sim}{x} - \underset{\sim}{Z}|} + Q \int \frac{\delta\rho(Z)d^3Z}{|\underset{\sim}{x} - \underset{\sim}{Z}|} + \delta W, \qquad (3-5)$$

where δW is the change in energy of the atom due to the perturbation $\delta\rho$. The first two terms of Eq. (3-5) are identified with the first two terms of Eq. (3-3). The last two terms of (3-5) are contained (but not separately exhibited) in the remaining terms of (3-3).[12]

The validity of the adiabatic approximation will be discussed below, and in Section IV means for evaluation of Eq. (3-2) will be considered.

For the high-energy approximation, we replace d by

$$d \simeq d_H = \epsilon_o + i\eta - \epsilon. \qquad (3-6)$$

In this approximation we may take ϵ as independent of the atomic state n and also as diagonal in the momentum p. Now, the coordinates $\underset{\sim}{Z}_1 \ldots \underset{\sim}{Z}_Z$ of the orbital electrons commute with d in F and consequently would appear only as parameters in F and V F if it were not for the operators P. These operators now occur only as projection operators however, and again one has a simple limit. The validity of this limit will be discussed below and application will be made in Section V.

We shall estimate the limits of validity of the high-energy and adiabatic approximations using the second-order term in $\mathcal{V}(0)$:

$$\mathcal{V}_2 \equiv \left\langle 0 \left| V \frac{1}{d} P V \right| 0 \right\rangle = \underset{n \neq 0}{\Sigma} \left\langle 0 | V | n \right\rangle \frac{1}{d(n)} \left\langle n | V | 0 \right\rangle , \qquad (3-7)$$

where d_n is the value of d when operating on ϕ_n. To carry out a specific discussion here and elsewhere in this paper, we shall assume Hartree-Fock wave functions for the atom - that is, we shall assume that the electrons have individual orbital states, $\phi_{n_\ell}(Z)$ with quantum number $n_\ell (\ell = 1, 2 \ldots Z)$. When convenient, we shall also use the Fermi-Thomas model to make semi-quantitative estimates.

Then, Eq. (3-7) is, in coordinate space,

$$\left\langle \underset{\sim}{x} | \mathcal{V}_2 | \underset{\sim}{x}' \right\rangle = \underset{\ell=1}{\overset{Z}{\Sigma}} \underset{n_\ell}{\Sigma} \int \phi_o^*(Z_\ell) V_\ell(\underset{\sim}{x} - \underset{\sim}{Z}_\ell) \phi_{n_\ell}(Z_\ell) \frac{1}{d} \phi_{n_\ell}^*(Z_\ell') V_\ell(\underset{\sim}{x}' - \underset{\sim}{Z}_\ell')$$

$$\times d_o(Z_\ell') d^3Z_\ell d^3Z_\ell' \qquad (3-8)$$

(See Eq. (2-3)). In momentum space this is

$$(\underset{\sim}{P}|\mathcal{V}_2|\underset{\sim}{P}') = \sum_{\ell=1}^{Z} \sum_{n_\ell} \int \frac{d^3P}{(2\pi)^3} \left[\int \phi_o^* (Z_\ell) \phi_{n_\ell}(Z_\ell) e^{-i(\underset{\sim}{p}-\underset{\sim}{P})\cdot \underset{\sim}{Z}_\ell} d^3 Z_\ell \right]$$

$$\frac{4\pi e'Q}{|\underset{\sim}{p}-\underset{\sim}{P}|^2} \quad \frac{1}{[\epsilon_o - \epsilon(P) + i\eta + W_o - W_{n_\ell}]} \quad \frac{4\pi e'Q}{|\underset{\sim}{p}'-\underset{\sim}{P}|^2}$$

$$\left[\int \phi_{n_\ell}^* (Z_\ell') \phi_o(Z_\ell') e^{-i(\underset{\sim}{p}'-\underset{\sim}{P})\cdot Z_\ell'} d^3 Z_\ell' \right] . \qquad (3\text{-}9)$$

As mentioned above, we are neglecting here the dependence of ϵ on the state n and considering ϵ to be diagonal in the state $\underset{\sim}{P}$. For the high-energy approximation this seems quite justifiable - indeed, in this case $\epsilon \simeq K$ should be adequate, as will appear from the following considerations.

The validity of the "high-energy" approximation depends upon having

$$|\epsilon - \epsilon_o| \gg (\overline{W_{n_\ell} - W_o}) , \qquad (3\text{-}10)$$

an appropriate average excitation energy of the atom. Now, we have

$$\epsilon - \epsilon_o \simeq \frac{P}{M} \delta p,$$

where δp is the momentum transferred to the scattered particle. To leave the atom excited, however, requires $\delta p \simeq p_F$, the Fermi momentum in the atom. Then, the condition (3-10) is

$$\frac{p}{M} \gg \frac{1}{p_F} (\overline{W_{n_\ell} - W_o}) . \qquad (3\text{-}11)$$

According to the Fermi-Thomas model,[16] the Fermi momentum is given by

$$p_F^2 = 2.2 \, Z^{4/3} \, \frac{\hbar^2}{a^2} \left[\frac{X(y)}{y} \right] ,$$

with

$$y \equiv \frac{Z^{1/3}}{0.9 \, a} \, r$$

and

$$a \equiv \frac{\hbar^2}{me^2} , \qquad\qquad (3\text{-}12)$$

where r is a distance measured from the center of the atom. The dimensionless function $X(y)$ is unity for $y \simeq 0$ and falls to zero for $y \gg 1$. For the energy $(\overline{W_{n_\ell} - W_o})$, we use the Fermi energy

$$\frac{p_f^2}{2m} = \frac{Z^{4/3} \, e^2}{0.9 \, a} \left[\frac{X(y)}{y} \right] .$$

If we square both sides of Eq. (3-11) and simplify, taking $\epsilon_o \simeq \frac{p^2}{2M}$, there results the condition

$$\epsilon_o \simeq \frac{p^2}{2M} \gg Z^{4/3} \left[\frac{M}{m} \right] \frac{e^2}{a} \left[\frac{X(y)}{y} \right] , \qquad\qquad (3\text{-}13)$$

if the high energy approximation is to be valid. Near the outer boundaries of the atom, $X(y)$ becomes small. In this case, we should more properly take

$$(\overline{W_{n_\ell} - W_o}) \simeq \frac{(\delta p)^2}{m} ,$$

where δp is the momentum transferred to an electron. If we assume the "size" of the atom to be approximately $a \, Z^{-1/3}$ the characteristic momentum transfer is

$$\delta p \simeq \frac{\hbar}{a} \, Z^{1/3} .$$

With this, Eq. (3-13) is replaced by the condition

$$\epsilon_o >> (\frac{M}{m}) \; Z^{2/3} \; e^2/a. \tag{3-14}$$

For the validity of the high-energy approximation, we require then that both conditions (3-13) and (3-14) be satisfied on the particles orbit.

We turn next to conditons for validity of the adiabatic approximation. For the moment, we ignore the possibility of rearrangement collisions. If we set

$$\frac{1}{d} = \frac{1}{W_o - W_n} + \frac{[\epsilon - \epsilon_0]}{[W_n - W_o][W_n - W_o + (\epsilon - \epsilon_o) - i\eta]} \quad , \tag{3-15}$$

the nonadiabatic correction is

$$\Delta \mathcal{V}_2 = \sum_{n \neq 0} \langle 0|V|n \rangle \; \frac{[\epsilon - \epsilon_o]}{[W_n - W_o][W_n - W_o + \epsilon - \epsilon_o - i\eta]} \; \langle n|V|0 \rangle \; . \tag{3-16}$$

Because $[\epsilon_o - \epsilon] \; \Psi_c = 0$, this may be written as

$$\Delta \mathcal{V}_2 = \sum_{n \neq 0} \langle 0|V|n \rangle \; \frac{1}{[W_n - W_o][W_n - W_o + \epsilon - \epsilon_o - i\eta]} \; \langle n|[\epsilon, V]|0 \rangle \; . \tag{3-17}$$

In the adiabatic limit, we have

$$[\epsilon, V] = -\frac{\hbar^2}{2M} \; \{ [\nabla^2 V] + 2(\nabla V) \cdot \nabla \} \; . \tag{3-18}$$

This results because in the adiabatic limit $\mathcal{V}(x)$ commutes with V.

When the scattered particle is well outside the atom and at $\underset{\sim}{x}$, the leading term in Eq. (3-18) is approximately

$$\frac{\hbar}{M} \; \frac{P}{x} \; V.$$

Then the value of $\Delta \mathcal{V}_2$ is

$$\Delta \mathcal{V}_2 \approx \mathcal{V}_2 \left[\frac{\hbar}{M} \; \frac{P}{x} \; \frac{1}{(W_n - W_o)} \right] \; . \tag{3-19}$$

We require then

$$\frac{\hbar}{x} \frac{P}{M} \ll \overline{(W_n - W_o)} \tag{3-20}$$

if the adiabatic limit is to be valid. Equation (3-20) is understandable from elementary considerations. The "collision time" is of the order of

$$\tau \simeq (x/P/M)^{-1}.$$

The uncertainty in energy during the collision is $\hbar/\tau$ which must be small compared to the excitation energy $\overline{(W_n - W_o)}$; this condition is equivalent to Eq. (3-20).

When the incident particle is inside the atom, we approximate the right-hand side of Eq. (3-18) by the first term and use Poisson's equation to write

$$[\epsilon, V] = -\frac{\hbar^2}{2M} \nabla^2 V = \frac{\hbar^2}{2M} 4\pi Q \sum_{\ell} \delta (\underset{\sim}{x} - \underset{\sim\ell}{Z}). \tag{3-21}$$

If Hartree-Fock wave functions are used to evaluate Eq. (3-17), we obtain (with the approximation (3-21))

$$\Delta \mathcal{V}_2 \simeq \sum_{\ell=1}^{Z} \sum_{n_\ell} \int V(\underset{\sim}{x} - \underset{\sim\ell}{Z}) \frac{4\pi e' Q \hbar^2}{2M [W_{n_\ell} - W_o]^2}$$

$$\times [\phi_{0_\ell}(\underset{\sim\ell}{Z}) \phi_{n_\ell}^*(\underset{\sim\ell}{Z}) \phi_{n_\ell}^*(\underset{\sim}{x}) \phi_0(x)] d^3 Z_\ell. \tag{3-22}$$

For very rough evaluation, we make the conservative estimate

$$\sum_{\ell=1}^{Z} \int V(\underset{\sim}{x} - \underset{\sim\ell}{Z}) \phi_{0_\ell}(\underset{\sim\ell}{Z}) \phi_{n_\ell}^*(\underset{\sim\ell}{Z}) d^3 Z_\ell, \simeq \mathcal{V}_1$$

where $\mathcal{V}_1$ is the second term on the right-hand side of Eq. (3-3). Also we have

$$\phi_0(x) \phi_{n_\ell}^*(x) \simeq \frac{1}{Z} n(x),$$

where n is the electron density in the atom. This is, by use of the Fermi-Thomas model,

$$\dot{n}(x) \simeq 0.1 \ Z^2/a^3 \ \left(\frac{X(y)}{y}\right)^{3/2} .$$

(3-23)

For $W_{n_\ell} - W_o$, we use again

$$\frac{Z^{4/3}}{0.9} \ e^2/a \ \left(\frac{X(y)}{y}\right) .$$

Then Eq. (3-22) becomes

$$\frac{\Delta \mathcal{V}_2}{\mathcal{V}_1} \simeq Z^{-5/3} \ \frac{m}{M} \ \left[\frac{y}{X(y)}\right]^{\frac{1}{2}} .$$

(3-24)

When rearrangement collisions may occur, the condition

$$| \epsilon - \epsilon_o | << \overline{(W_n - W_o)}$$

will not in general be satisfied at the time the rearrangement occurs. It is then necessary that the propagators d^{-1} be expressed in terms of new eigenvalues W_n and ϵ appropriate to the new atomic systems. When this is done, our formalism applies to those new systems. The potential $\mathcal{V}$ has an imaginary part in this case, however. To first order this is

$$\text{Im}[\mathcal{V}] = \text{Im} \ [\ \Sigma_n \ \langle 0|V|n \rangle \ \frac{1}{d} \ \langle n|V|0 \rangle \ ].$$

(3-25)

The value in this approximation is given essentially by the quantity R of Eq. (2-20):[17]

$$\text{Im}[\mathcal{V}] = -\frac{i}{2} \ R.$$

(3-26)

IV. THE ADIABATIC APPROXIMATION FOR $\mathcal{V}$

In this Section we should like to discuss more completely the adiabatic form of $\mathcal{V}$. This means estimating the effect of the higher-order terms in Eq. (3-3). As we shall indicate, an adequate evaluation seems feasible if one uses Hartree-Fock wave functions. The principal reason for this is that the inner-shell electrons are sufficiently tightly bound that they do not polarize very readily. Thus the major contribution from higher-order terms in Eq. (3-3) comes from only the outermost electron (or electrons). Our method permits us to study this in detail.

To orient ourselves, we first discuss the Fermi-Thomas model. The electron density n(r) is then

$$n(r) = \frac{8\pi}{3h^3} \ [2me\phi]^{3/2}, \tag{4-1}$$

where ϕ is the electric potential, as given by Poisson's equation:

$$\nabla^2 \phi = -4\pi e \ [Z\,\delta(x) - n(\underline{r})]. \tag{4-2}$$

The Fermi momentum p_F is related to ϕ and n by

$$\frac{1}{2m} \ p_F^{\ 2} = e\phi$$

and

$$\frac{8\pi}{3h^3} \ p_F^{\ 3} = n \tag{4-3}$$

(thus Eq. (4-1)).

We next ask for the modification of ϕ and n when an external charge of density S(r) is placed within the atom. To first order in S, we write

$$\phi = \phi_o + \phi'$$

and

$$n = n_o + n' \ ,$$

where, from Eq. (4-1), we have

$$n' = \frac{4\pi}{h^3} \ (2me)^{3/2} \ \phi_o^{\ 1/2} \ \phi'. \tag{4-4}$$

Now Eq. (4-2) becomes

$$(\nabla^2 - \frac{1}{\lambda_D^2}) \ \phi' = -4\pi S \tag{4-5}$$

and

$$\frac{1}{\lambda_D^2} \simeq \frac{4}{\pi} \frac{p_F}{\hbar} \frac{1}{a} \quad . \qquad (4\text{-}6)$$

The "radius" of the atom is

$$b \simeq 0.9 \ a \ Z^{-1/3}, \qquad (4\text{-}7)$$

while the shielding distance λ_D, as given by Eq. (4-6), is

$$\lambda_D \simeq \sqrt{\pi/8} \ a \ Z^{-1/3} \quad . \qquad (4\text{-}8)$$

Because these two distances are comparable, we conclude that complex cooperative motions are not of predominant importance to our problem and that perturbation methods may therefore be applicable.

With the Fermi-Thomas model, one may evaluate Eq. (3-5) as follows:

$$\mathcal{V} \simeq \frac{ZeQ}{x} - eQ \int \frac{n_0(r) \ d^3 r}{|x - r|} - e \int n'(r) \ \phi'(r) \ d^3 r. \qquad (4\text{-}9)$$

The last term represents the "polarization energy". From Eqs. (4-4) and (4-5), we obtain (for Q near the center of the atom)

$$\phi' = \frac{Q}{r} \ e^{-r/\lambda_D}$$

and

$$en' = \frac{1}{\pi^2} \frac{me^2}{\hbar^2} \frac{p_F}{\hbar} \phi',$$

and therefore

$$e \int n'(r) \phi'(r) d^3 r \simeq \frac{1.5}{\pi^2} \frac{Q^2}{a} Z^{1/3} \int d^3 y \ \left(\frac{X(y)}{y}\right)^{\frac{1}{2}} e^{-2y} \quad . \qquad (4\text{-}10)$$

The notation of Eq. (3-12) has been used here.

The order of magnitude of the terms in Eq. (4-9) is now easily seen. First, the total binding energy[16] of the neutral atom is

$$E_T \simeq e^2/a \ Z^{7/3}.$$

The first and second terms in Eq. (4-9) are of magnitude

$$E_Q \simeq \frac{e^2}{a} Z^{4/3} . \qquad (4\text{-}11a)$$

Finally, the energy of the last term in (4-9) is

$$E_P \simeq \frac{e^2}{a} Z^{1/3} . \qquad (4\text{-}11b)$$

We now return to the quantum mechanical Eq. (3-2) for $\mathcal{V}$. The second order energy is

$$\mathcal{V}_2 = \left\langle 0 | V \frac{1}{d_A} V | 0 \right\rangle . \qquad (4\text{-}12)$$

Now, in the "classical limit", if the charge Q is in the interior of the atom, we have

$$V \simeq \frac{e^2}{b} \simeq \frac{e^2}{a} Z^{1/3}$$

and

$$(-d_A) \simeq Z^{4/3} \frac{e^2}{a} .$$

Finally, we have

$$\sum_{\text{electrons}} [\left\langle 0 | \right] [| 0 \rangle] \simeq \int d^3x \, n(x) \approx Z.$$

Thus we can write

$$\mathcal{V}_2 \simeq Z \left[\frac{e^2}{b} \right]^2 \left[Z^{4/3} \frac{e^2}{a} \right]^{-1} = Z^{1/3} \frac{e^2}{a} . \qquad (4\text{-}13)$$

This agrees with Eq. (4-11b).

A more conventional calculation of this (Eq. 4-13) may be made if we consider the electrons as uniformly distributed in plane-wave states in a box of volume

$$\tau = \frac{4\pi}{3} b^3 .$$

The electron levels are filled to the Fermi momentum P_F. Now, Eq. (4-12) is

$$\mathcal{V}_2 = \frac{(4\pi e^2)^2}{\tau^2} \int_{P_o < P_F} \tau \, d^3 P_o \int_{P > P_F} \tau \, d^3 P \, \frac{1}{[(P_o - P)^2]^2} \, \frac{2m}{P_o^2 - P^2}$$

$$\simeq (4\pi e^2)^2 \, m P_F \int_0^{P_F} \frac{dP_o}{(P_o - P_F)^2} . \qquad (4\text{-}12a)$$

Although this integral diverges, the second-order perturbation $\mathcal{V}_2$ does not. This is because the states in a box are discrete rather than continuous. The gap between levels is

$$\Delta \simeq \frac{\hbar}{b} \quad .$$

Thus the integral above (4-12a) should be replaced by

$$\int_0^{P_F - \Delta} \frac{dP_o}{(P_o - P_f)^2} \simeq \frac{1}{\Delta} = \frac{b}{\hbar} \quad .$$

This gives

$$\mathcal{V}_2 = (4\pi e^2)^2 \, m P_f \, \frac{b}{\hbar} = \frac{e^2}{a} \, Z^{1/3} \quad . \tag{4-14}$$

This, of course, agrees with Eqs. (4-11b) and (4-13).

The higher-order perturbation terms in Eq. (3-2) are of the form

$$V \frac{1}{d_A} PV \frac{1}{d_A} PV + V \frac{1}{d_A} PV \frac{1}{d_A} PV \frac{1}{d_A} PV + \ldots \quad . \tag{4-15}$$

The P operator plays a very important role in determining the convergence of this series. The reason for this is that because of P each interaction V must change the electronic states. Because the Fermi-momentum is large, this implies a tendency toward large values of d_A.

If the terms $[\mathcal{V}(0) - \mathcal{V}(n)]$ in (3-1a) are negligible, then the condition for the convergence of the series (4-15) seems fairly simple. Using the above model of a degenerate Fermi gas in a box of volume $\frac{4\pi}{3} b^3$, we see that each electron that scatters must scatter at least twice - once when it is excited and once when it is de-excited. Now, an excitation followed by a de-excitation contributes approximately

$$\frac{1}{d_A} \left\langle 0 \left| V \frac{1}{d} V \right| 0 \right\rangle$$

$$\simeq \frac{1}{d_A^2} \left(\frac{4\pi e Q}{P_F^2} \right)^2 \left(\frac{Z}{\tau} \right) \left[P_F^3 \right] \quad . \tag{4-16}$$

If we set $d_A \simeq \frac{e^2}{a} Z^{4/3}$, the expression (4-16) is

$$\frac{e^2}{a} \; \frac{1}{\frac{e^2}{a} Z^{4/3}} \simeq Z^{-4/3}.$$

The expansion (4-15) thus is an expansion of the form

$$E \simeq \mathcal{V}_2 [1 + a_1 Z^{-4/3} + a_2 Z^{-8/3} + a_3 Z^{-12/3} + \dots] \; .$$

$$(4-17)$$

Here the coefficients a_1, a_2 --- are independent of Z.

This argument suffers from a flaw, however. If there is a close approach of two levels as we vary the parameter $\underset{\sim}{x}$, then d_A becomes small. This may be associated with the possibility of a rearrangement collision. Such contributions must be included separately and in addition to the "well-behaved" series (4-17) (this condition is described in the Appendix).

When the scattered particle is at large distances from the atom, the series (3-3) is again simple. The first two terms cancel, and one is left with

$$\mathcal{V} = \left\langle 0 \middle| V \frac{1}{d_A} PV \middle| 0 \right\rangle + \left\langle 0 \middle| V \frac{1}{d_A} PV \frac{1}{d_A} PV \middle| 0 \right\rangle + \dots \; .$$

$$(4-18)$$

As may be easily seen, the term with q factors of V varies as X^{-2q} (because of the operators P).

That is, we have

$$V = \frac{Ze'Q}{x} - \sum_{\ell=1}^{Z} \frac{e'Q}{x^2} (\hat{\underset{\sim}{x}} \cdot \underset{\sim}{Z}_\ell) + \dots \; . \tag{4-19}$$

The first term here makes no contribution to the terms in the series (4-18). The second-order potential above is thus

$$\mathcal{V}_2 = \left\langle 0 \middle| V \frac{1}{d_A} PV \middle| 0 \right\rangle = - \frac{Q^2 e^2}{x^4} \sum_{n \neq 0} \frac{|\langle n | \hat{\underset{\sim}{x}} \cdot \sum_\ell \underset{\sim}{Z}_\ell | 0 \rangle|^2}{W_n - W_o} \; .$$

$$(4-20)$$

This may be related to the induced electric dipole moment of the atom

$$\underset{\sim}{D} = \alpha \underset{\sim}{E} , \tag{4-21}$$

where α is the polarizability and $\underset{\sim}{D}$ is the dipole moment. The polarizability of the atom is easily seen to be (see Eq. (4-20))

$$\alpha = 2e^2 \sum_{n \neq 0} \frac{|\langle n| \underset{\sim}{\hat{x}} \cdot \underset{\ell}{\sum} \underset{\sim}{\dot{z}_\ell} |0 \rangle|^2}{W_n - W_o} \tag{4-22}$$

Thus, we have the familiar classical result,

$$\mathcal{V}_2 = - \frac{Q^2 \alpha}{2x^4} \equiv \frac{-P}{x^4} . \tag{4-23}$$

The conditions for the validity of the adiabatic approximation in this case have been discussed in Section III.

Atomic polarizabilities have been evaluated particularly by Sternheimer.[18]

When the scattered particle is close to the outer edge of the atom, the polarization due to the outer-shell electrons is less easily calculated. In Section VI, we shall suggest variational methods for handling this problem.

V. APPLICATION TO HYDROGEN

We now turn to the application to hydrogen of the method described in Sec. II. In this case the statistical methods of Sec. II and III do not apply, but the wave functions and eigenvalues of the atomic system are explicitly known so that evaluation of the scattering potential is again possible in the limits discussed above. We again limit our discussion to the case where the nuclear-recoil velocity is small compared to the electron velocity so that the discussion of Sec. II may be repeated and Eqs. (2-19) applied directly. We shall discuss only the first two orders in the expansion of the elastic scattering potential

$$\mathcal{V}(x) = V_N(x) + \langle 0| V |0 \rangle + \langle 0| V \frac{1}{d} PV |0 \rangle . \tag{5-1}$$

As before, the first two terms represent the nuclear coulomb potential shielded by the atomic electron. These may be evaluated explicitly by the use of the ground-state hydrogen wave function, $\phi_o(z) = e^{-z/a}\sqrt{\pi a^3}$, which yields

$$\mathcal{V}_1(x) = V_N(x) + \langle 0|V|0 \rangle = eQ\left(\frac{1}{x} + \frac{1}{a}\right)e^{-2x/a}. \qquad (5-2)$$

The second-order $\mathcal{V}_2$ represents an impulsive scattering by the electron, with the atom going into an intermediate excited state, while the scattered particle moves in the potential of that atomic state, $\mathcal{V}(n)$. Another impulsive scattering then takes place de-exciting the atom. In general $\mathcal{V}_2$ is an energy-dependent nonlocal potential

$$\mathcal{V}_2(\underset{\sim}{x}, \underset{\sim}{x}') = e^2 Q^2 \sum_{n\neq 0} \sum_{a} \int \phi_o^*(\underset{\sim}{Z}) \frac{1}{|\underset{\sim}{Z}-\underset{\sim}{x}|} \phi_n(\underset{\sim}{Z}) \frac{\psi_a(\underset{\sim}{x},n)\psi_a^*(\underset{\sim}{x}',n)}{[\epsilon_o - \epsilon_{a,n} + W_o - W_n + i\eta]}$$

$$\phi_n^*(\underset{\sim}{Z}') \frac{1}{|\underset{\sim}{Z}'-\underset{\sim}{x}'|} \phi_o(\underset{\sim}{Z}') \, d^3Z \, d^3Z', \qquad (5-3)$$

where $\psi_a(x,n)$ is the ath eigen-function and ϵ_{an} is the energy of the scattered particle moving in the potential of the atom in its nth state.

In the limit of large distances, the potential changes by a small fraction in a wave length, and the conditions for adiabaticity apply. Then the approximate Eq. (3-1b) may be used, so that the dependence of the denominator on the scattered particle index a disappears, and the sum over a may be performed by the use of the completeness relation for the wave functions ψ_K. The potential $\mathcal{V}_2$ is then local,

$$\mathcal{V}_2(\underset{\sim}{x}, \underset{\sim}{x}') = -e^2 Q^2 \delta(\underset{\sim}{x}-\underset{\sim}{x}') \sum_{n\neq 0} \int \frac{d^3Z \, d^3Z'}{|\underset{\sim}{Z}-\underset{\sim}{x}||\underset{\sim}{Z}'-\underset{\sim}{x}|} \frac{\phi_o^*(\underset{\sim}{Z})\phi_n(\underset{\sim}{Z}) \, \phi_n^*(\underset{\sim}{Z}') \, \phi_o(\underset{\sim}{Z}')}{(W_n - W_o)},$$

$$(5-4)$$

and real so that only elastic scatterings are possible. At large distances, we again make the expansion of Eq. (4-19). The contribution of the leading term is the dipole polarizability

$$\mathcal{V}_2 = -\frac{Q^2}{x^4} \frac{a}{2} \quad , \qquad (5\text{-}5a)$$

where we have

$$a = + \frac{2e^2}{3} \sum_{n \neq 0} \frac{|\int d^3Z \, \phi_o^*(\underset{\sim}{Z}) \, \underset{\sim}{Z} \, \phi_n(\underset{\sim}{Z})|^2}{W_n - W_o} \quad . \qquad (5\text{-}5b)$$

This can be evaluated analytically with the result $a = \frac{9}{2} a_o^3$.[18] In a similar manner one can show that the qth term in the series behaves like X^{-2q}.[19]

In the adiabatic limit we can find the scattering potential at small distances from the proton by noting that it is essentially given as an energy eigenvalue of the atom in the field of the scattered particle (See Eq. 6-4). Thus, if the scattered particle, with charge Q, is at the position of the proton the atomic electron is then moving in the coulomb field of a charge $e + Q = Ze$. For $Z > 0$ the eigenvalue for such a system is well known[20] to be $Z^2 W_o$. The adiabatic potential at the origin is then given by

$$\lim_{x \to 0} \left(\mathcal{V}_o(x) - \frac{eQ}{x} \right) = \mathcal{V}(0) = (Z^2 - 1) W_o. \qquad (5\text{-}6)$$

For example, for a singly charged, negative-scattered particle we have $Z = 0$ and $\mathcal{V}(0) = \frac{e^2}{2a}$. The potential can be obtained from a variational principle (see Eqs. 6-8) and be put in a form suitable for negative Qx (Eq. (6-13)). For this form we use for $\mathcal{V}_1$ the interaction with the static electron cloud,

$$\mathcal{V}_1(x) = \frac{4\pi e}{x} \int_0^x x'^2 \, dx' \, \rho(x') + 4\pi e \int_x^\infty x' \, dx' \, \rho(x')$$

$$= -\frac{e^2}{a} [e^{-2x/a} - \frac{a}{x}(1 - e^{-2x/a})] \quad , \qquad (5\text{-}7)$$

and we modify the polarization potential in the manner suggested by Bates and Massey,[3]

$$\mathcal{V}_P = \frac{P}{(\underset{\sim}{d}^2 + x^2)^2} \quad . \tag{5-8}$$

The parameter $\underset{\sim}{d}$ is determined by the condition on $\mathcal{V}(0)$ to be

$$\underset{\sim}{d} = \left(\frac{Pa}{e^2}\right)^{\frac{1}{4}} = \sqrt{3/2} \ a. \quad \text{Then the approximate potential is}$$

$$\mathcal{V}(x) = \frac{[\mathcal{V}_1(x)]^2}{\mathcal{V}_1(x) + \dfrac{P}{(\underset{\sim}{d}^2 + x^2)^2}} \quad . \tag{5-9}$$

For a positive particle the variational form (Eq. 6-13) is not suitable, but we may construct an approximate potential from the requirements that $\mathcal{V}(0) = 3W_o = -3/2 \ e^2/a$ and from the form of the polarization potential. For a positive charge, the potential is

$$\mathcal{V}_1(x) = \frac{e^2}{a} \left[e^{-2x/a} - \frac{a}{x} (1 - e^{-2x/a}) \right]. \tag{5-10}$$

For the polarization potential (Eq. 5-8) we again use the form

$$\mathcal{V}(x) = \mathcal{V}_1(x) - \frac{P}{(\underset{\sim}{d}^2 + x^2)^2} \quad , \tag{5-11}$$

where

$$\underset{\sim}{d} = \left(\frac{2pa}{e^2}\right)^{\frac{1}{4}} = \left(\frac{9}{2}\right)^{\frac{1}{4}} \ a$$

is again determined from the condition at the origin.

We may estimate the magnitude of the nonadiabatic contribution to $\mathcal{V}_2$ by substituting Eq. (3-15) in Eq. (5-3):

$$\Delta\mathcal{V}_2 = -e^2 Q^2 \sum_{n \neq 0} \sum_a \int d^3Z \, d^3Z' \, \phi_o(\underset{\sim}{Z}) \frac{1}{|\underset{\sim}{Z} - \underset{\sim}{x}|} \phi_n(\underset{\sim}{Z}) \frac{\epsilon_o - \epsilon_n}{(W_n - W_o)^2}$$

$$\psi_a(\underset{\sim}{x}, n) \, \psi_a^*(\underset{\sim}{x}', n) \, \phi_n^*(\underset{\sim}{Z}') \frac{1}{|\underset{\sim}{Z}' - \underset{\sim}{x}'|} \phi_o(\underset{\sim}{Z}'), \tag{5-12}$$

where we have

$$\epsilon_n = -\frac{\hbar^2}{2M} \nabla^2 + \mathcal{V}(n).$$

We neglect the n dependence of ϵ_n and perform the sum over n. In the limit of large distances, we find

$$\Delta \mathcal{V}_2 \simeq -e^2 Q^2 (\epsilon_o - \bar{\epsilon}_n) \ \frac{\delta(\underset{\sim}{x} - \underset{\sim}{x}')}{x^4} \ \frac{1}{3} \sum_n \frac{|\int d^3 Z \, \phi_o(Z) \, \underset{\sim}{Z} \, \phi_n(\underset{\sim}{Z})|^2}{(W_n - W_o)^2}$$

$$(5-13)$$

This gives

$$\Delta \mathcal{V}_2 \simeq -\frac{e^2 Q^2}{2M} \ \beta \ \left(\frac{6\hat{x} \cdot P_o}{x^5} + \frac{12}{x^6} \right) \quad , \qquad (5-14)$$

where we have

$$\beta = \frac{1}{3} \sum_n \frac{|\int d^3 Z \, \phi_o(Z) \, \underset{\sim}{Z} \, \phi_n(\underset{\sim}{Z})|^2}{(W_n - W_o)^2} \ = \ O\left(\frac{a^4}{a^2}\right) \quad . \qquad (5-15)$$

Thus

$$\frac{\Delta \mathcal{V}_2}{\mathcal{V}_2} \simeq \left(\frac{m}{M}\right) \left[\left(\frac{a}{x}\right)^2 \quad \text{and} \quad \left(\frac{a}{x}\right)\left(\frac{a \, P_o}{\hbar}\right) \right] << 1$$

defines the region of validity of the adiabatic approximation.

In the high-energy limit, the momentum transfer to the atomic system is assumed to be large compared to the important momenta of the electron, and small compared to the initial momentum of the scattered particle. In this case the potential expression again becomes simple. We approximate the intermediate states, $\psi_a(\underset{\sim}{x}, n)$, by free states and write in the momentum representation

$$\langle P' | \mathcal{V}_2 | P_o \rangle = 4e^2 Q^2 \sum_{n \neq 0} \int \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} \ d^3 q \ \frac{e^{i(P_o - q) \cdot x_1 + i(q - P') \cdot x_2}}{(q - P_o)^2 (q - P')^2}$$

$$\times \ \frac{\phi_o(x_1) \phi_n(x_1) \phi_n^*(x_2) \phi_o(x_2)}{[\epsilon_o - \epsilon(q) + W_o - W_n + i\eta]} \quad . \qquad (5-16)$$

In the high-energy limit, we approximate the denominator by neglecting its dependence upon the energy change of the bound electrons. This may be justified by noting that

$$\epsilon_o - \epsilon(q) \sim \frac{P_o \delta P}{M}$$

while

$$W_o - W_n \sim \frac{\delta P^2}{2M}$$

(as in Sec. III). Further, we may approximate the energy of the scattered particle by its kinetic energy only $\epsilon(q) = q^2/2M$. The sum over excited states may now be performed by the use of the completeness relation

$$\sum_{n \neq 0} \phi_n(\underset{\sim}{x}_1) \phi_n^*(\underset{\sim}{x}_2) = \delta(\underset{\sim}{x}_1 - \underset{\sim}{x}_2) - \phi_o(\underset{\sim}{x}_1) \phi_o(\underset{\sim}{x}_2) \quad . \qquad (5-17)$$

The spatial integrations are now performed by the use of

$$\int d^3x \, \phi_o^2(x) \, e^{i\underset{\sim}{P} \cdot \underset{\sim}{x}} = \frac{(2/a)^4}{[(2/a)^2 + P^2]^2} \qquad (5-18)$$

We then have

$$Re \left\langle P' | \mathcal{U}_2 | P_o \right\rangle = \frac{2e^2 Q^2 M}{a^4 \pi^6} \, Re \int \frac{d^3q}{(\underset{\sim}{q} - \underset{\sim}{P}_o)^2 (\underset{\sim}{q} - \underset{\sim}{P}')^2 (P_o^2 - q^2 + i\eta)}$$

$$\left\{ \frac{1}{[(2/a)^2 + (\underset{\sim}{P}_o - \underset{\sim}{P}')^2]^2} - \frac{(2/a)^4}{[(2/a)^2 + (\underset{\sim}{P}_o - \underset{\sim}{q})^2]^2 \, [(2/a)^2 + (\underset{\sim}{P}' - \underset{\sim}{q})^2]^2} \right\} \quad .$$

$$(5-19)$$

Now let us take

$$\underset{\sim}{P} = \frac{\underset{\sim}{P}_o + \underset{\sim}{P}'}{2} \quad , \quad \underset{\sim}{\delta} = P' - \underset{\sim}{P}_o, \quad \text{and} \quad \underset{\sim}{y} = q - \underset{\sim}{P}.$$

Then we have

$$\text{Re}\left\langle P' | \mathcal{V}_2 | P_o \right\rangle = \frac{2e^2Q^2M}{a^4\pi^6} \text{Re} \int \frac{d^3y}{(\underset{\sim}{y} - \frac{\delta}{2})^2 (\underset{\sim}{y} + \frac{\delta}{2})^2 [2\underset{\sim}{y}\cdot\underset{\sim}{P} - y^2 + i\eta]}$$

$$\left\{ \frac{1}{[(2/a)^2 + \delta^2]^2} - \frac{(2/a)^4}{[(2/a)^2 + (\underset{\sim}{y} + \frac{\delta}{2})^2]^2 \ [(2/a)^2 + (\underset{\sim}{y} - \frac{\delta}{2})^2]^2} \right\}$$

$$(5\text{-}20)$$

But $P\cdot\delta$ equals 0, so that the integral is a function of only the magnitude of the vectors $\underset{\sim}{\delta}$ and $\underset{\sim}{P}$. We may then average over the directions of P and expand in $\frac{1}{P}$. The remaining integral may then be performed with the result

$$\text{Re}\left\langle P' | \mathcal{V}_2 | P_o \right\rangle = \frac{-e^2Qa}{128\pi^4\epsilon_o} \left\{ \frac{\pi}{\gamma(1+\gamma^2)^2} + \frac{2}{\gamma}\left(\sin^{-1}\frac{\gamma^2-1}{\gamma^2+1} - \sin^{-1}\frac{\gamma}{\sqrt{4+\gamma^2}} \right) \right.$$

$$\left. + \frac{6}{(\gamma^2+1)(\gamma^2+4)} - \frac{2}{(\gamma^2+4)^2} \right\} , \qquad (5\text{-}21)$$

where $\gamma = a\delta/2\hbar = a/2\hbar \ |\underset{\sim}{P'} - \underset{\sim}{P}_o|$. For large δ this takes the form

$$\text{Re}\left\langle P' | \mathcal{V}_2 | P_o \right\rangle = \frac{-e^2Q^2}{4\pi^3\epsilon_o a^4\delta^5} . \qquad (5\text{-}22)$$

In coordinate space, we may obtain the behavior of the local potential $\mathcal{V}_2(x)$ near the origin by transforming Eq. 5-16. The result is

$$\mathcal{V}_2(x) = \frac{-e^2Q^2}{16\pi^2 a^2\epsilon_o} \left[1 + \frac{8}{3}\left(\frac{x}{a}\right)^2 \left(\frac{1}{2} + \ln\frac{x}{2a}\right) + \ldots \right] . \qquad (5\text{-}23)$$

This may be combined with the large-distance potential (Eq. 5-5) to give the approximate high-energy potential:

$$\mathcal{V}_2(x) = \frac{-\dfrac{e^2Q^2}{16\pi^2 a^2 \epsilon_o}\left[1 + \dfrac{8}{3}\left(\dfrac{x}{a}\right)^2\left(\dfrac{1}{2} + \ln\dfrac{x}{2a}\right)\right]}{1 + \dfrac{2}{27\pi^2}\dfrac{e^2}{a\epsilon_o}\left(\dfrac{x}{a}\right)^6\left(\dfrac{1}{2} + \ln\dfrac{x}{2a}\right)} \ .$$

(5-24)

We may estimate the range of validity of the high-energy approximation by using

$$\frac{1}{d} = \frac{1}{\epsilon_o - \epsilon(q)} + \frac{W_n - W_o}{(\epsilon_o - \epsilon(q))^2} + \ldots$$

(5-25)

in Eq. 5-11 and estimating the contribution of the second term. We approximate $W_n - W_o$ by some average excitation energy and perform the integrals in the manner described in connection with Eq. 5-15. The result is

$$\frac{\Delta\mathcal{V}_2}{\mathcal{V}_2} \simeq \frac{M}{m}\left(\frac{\hbar}{a\delta}\right)^2 << 1$$

(5-26)

as a requirement for the validity of the high-energy approximation.

VI. VARIATIONAL PRINCIPLES

It is possible to formulate a number of variational principles for use in obtaining the potential $\mathcal{V}$. These result from the use of the integral equation in terms of which $\mathcal{V}$ may be expressed. We begin by discussing the simpler adiabatic approximation.

A. The Adiabatic Limit

In the adiabatic limit we have:

$$\mathcal{v}(0) = \langle 0 | VF | 0 \rangle \quad , \quad \mathcal{V}(n) = \langle n | VF | n \rangle$$

$$F = 1 + \frac{1}{d_A} \, PVF$$

$$d_A = W_0 + \mathcal{v}(0) - (H_A + \mathcal{v}). \tag{6-1}$$

Here we have set $\mathcal{v}(0) = \mathcal{V}(0) - \frac{ZeQ}{x}$. The term $\frac{ZeQ}{x}$ may evidently be omitted from our considerations here.

The equation for F may be rewritten in the original form

$$F = 1 + \frac{1}{d_A} \, VF - \frac{1}{d_A} \, (1-P) \, VF$$

$$= 1 + \frac{1}{d_A} \, (V - \mathcal{v}) \, F. \tag{6-2}$$

Now, set

$$\Phi \equiv F | 0 \rangle \tag{6-3}$$

and operate on both sides of (6-2) with d_A. This leads to

$$[H_A + V] \, \Phi = (W_0 + \mathcal{v}_0) \, \Phi. \tag{6-4}$$

Thus Φ satisfies the Schrödinger equation for the atom in the potential of the scattered particle. Equation (6-4) is, of course, not unexpected.

In view of Eq. (6-4), which shows that $\mathcal{v}_0$ is given by a standard Schrödinger eigenvalue equation, we may generalize Eqs. (6-1). Using the expressions of Riesenfeld and Watson,[21] we have (where $\mathcal{O}$ is essentially an arbitrary operator):

$$\mathcal{V}(0) = \lim_{\Delta E \to \mathcal{V}(0)} \left\langle 0 | VM | 0 \right\rangle$$

$$M = 1 + \frac{1}{b - \mathcal{O}} (V - \mathcal{O}) M$$

$$\left\langle 0 | M | 0 \right\rangle = 1, \quad b \equiv W_o + \Delta E - H_A$$

$$\Phi \equiv M | 0 \rangle .$$ (6-5)

With Eq. (6-4), we may apply standard variational methods. That which has been most commonly used is the Hartree-Fock method.[22] This involves considerable computational labor. A simpler, less elaborate approach has been used by Buckingham in discussing atomic polarizabilities.[2] He begins with the minimal expression

$$(W_o + \mathcal{V}(0)) = \frac{\int \Phi^*(H_A + V)\Phi \, d\tau}{\int \Phi^* \Phi \, d\tau}$$ (6-6)

Choosing parametrized trial forms for Φ, Buckingham obtains an expression for the polarization energy $\mathcal{V}(0)$.

In addition to these, there is a class of useful variational expressions that seem to have originated with Schwinger.[13] We illustrate these with an example.

Consider the Brillouin-Wigner form of Eqs. (6-5):

$$\Phi = \chi + \frac{1}{b} [1 - \Lambda_o] V \Phi,$$ (6-7)

where $\chi \equiv | 0 \rangle$ and Λ_o is a projection operator onto the state $| 0 \rangle \equiv \chi$. Then the expression

$$\mathcal{V}_T = \frac{(\chi_1 V \Phi_1)(\Phi_2, V \chi)}{(\Phi_2, [V - V\frac{1}{b}(1 - \Lambda_o)V] \Phi_1)}$$ (6-8)

reduces to $\mathcal{V}_o$ when we have

$$\Phi_1 = \Phi_2 = \Phi .$$ (6-9)

Furthermore, $\mathcal{V}_T$ is stationary with respect to independent, small variations of Φ_1 and Φ_2 about the correct values (6-9). To see this, we write

$$\Delta_o \equiv (\Phi_2 \; [V - V \frac{1}{b} \; (1 - \Lambda_o)V] \; \Phi_1). \tag{6-10}$$

Then, varying Φ_2, we obtain

$$\delta \mathcal{V}_T = \frac{(\chi, V\Phi_1)(\delta\Phi_2 V\chi)}{\Delta_o} - \frac{1}{\Delta_o^2} \; (\chi, V\Phi_1)(\Phi_2, V\chi)(\delta\Phi_2, V\chi) \; . \tag{6-11}$$

On setting $\Phi_1 = \Phi_2 = \Phi$, we obtain

$$(\chi, V\Phi) = (\Phi, V\chi) = \Delta_o .$$

Thus $\delta \mathcal{V}_T = 0$. In the same manner, one may vary Φ_1 to obtain $\delta \mathcal{V}_T = 0$.

To illustrate Eq. (6-8), let us set $\Phi_1 = \Phi_2 = \chi$. Then

$$(\chi, V \frac{1}{b} (1 - \Lambda_o) V\chi) = - \frac{p}{x^4} \tag{6-12}$$

is the polarization potential obtained in Section IV [Eq. (4-23)]. Similarly,

$$\mathcal{V}_1(x) \equiv (\chi, V\chi)$$

is the average potential associated with the electrons in the unperturbed atom. This is usually calculated using Hartree or Hartree-Fock wave-functions. Then, Eq. (6-8) becomes

$$\mathcal{V}_o \simeq \mathcal{V}_T = \frac{[\mathcal{V}_1^{\ell}(x)]^2}{\mathcal{V}_1^{\ell}(x) + \frac{p}{x^4}} \; . \tag{6-13}$$

Equation (6-13) is suitable for negative Q. It breaks down (i.e., the denominator vanishes at some distance x) for positive Q. This breakdown is related to the fact that the energy may be lowered if the positive charge actually captures an orbital electron. In the case of a positive charge Q, one cannot of course use the asymptotic form $(-\frac{p}{x^4})$ of Eq. (6-12), and the

singularity will only occur if the polarization term is larger in magnitude than is $\mathcal{V}_1(x)$ for some value of x. This is associated with the crossing of levels, as discussed in Section IV.

B. The General Case

Even when the adiabatic approximation is not valid, a variational principle may be given. Consider the wavefunction

$$\psi^{(+)} = \chi + \frac{1}{d} \, PV\psi^{(+)} , \tag{6-14}$$

where we now write

$$\mathcal{V}(0) \equiv \mathcal{V}(0) - \frac{ZeQ}{x} \quad \text{(in general)}$$

so that

$$\mathcal{V}(0) = (\chi, V\psi^{(+)}). \tag{6-15}$$

Next introduce

$$F^{(-)} = 1 + \frac{1}{d^+} \, P^+ \, VF^{(-)} \tag{6-16}$$

and

$$\psi^{(-)} = F^{(-)}\chi. \tag{6-17}$$

The symbol P^+ is defined by the requirement

$$F^{(-)+} = 1 + F^{(-)+} \, V \frac{1}{d} \, P. \tag{6-18}$$

Now,

$$F^{(-)+} \, V \equiv \mathcal{G} \tag{6-19}$$

satisfies the equation

$$\mathcal{G} = V + \mathcal{G} \frac{1}{d} \, PV. \tag{6-20}$$

It also satisfies the equation

$$\mathcal{G} = V + VP \frac{1}{d} \, \mathcal{G} , \tag{6-21}$$

as may be verified by substitution. Because of Eq. (6-21), we have then

$$F^{(-)+} \, V = VF, \tag{6-22}$$

and therefore,

$$\mathcal{V} = (\psi^{(-)}, V \phi_o). \tag{6-23}$$

It follows then that the potential is

$$\mathcal{V} = \frac{(\phi_o, V\psi^{(+)})(\psi^{(-)}, V\phi_o)}{(\psi^{(-)}, [V - V\frac{1}{d} PV]\psi^{(+)})} .$$ (6-24)

Following the argument of Eq. (6-11), we can easily show that Eq. (6-24) is stationary with respect to small, independent variations of $\psi^{(-)}$ and $\psi^{(+)}$.

An immediate application of Eq. (6-24) is that of obtaining non-adiabatic corrections to the adiabatic potential. Write, for some trial $\psi^{(-)}$ and $\psi^{(+)}$,

$$(\psi^{(-)}, [V - V\frac{1}{d} PV]\psi^{(+)}) \equiv \Delta_o + \Delta_1 .$$ (6-25)

Here Δ_o is the adiabatic form (6-10) and Δ_1 represents the correction to this. Then we have

$$\mathcal{V} = \frac{[\mathcal{V}_A]^2}{\Delta_o} [1 - \frac{\Delta_1}{\Delta_o + \Delta_1}] .$$ (6-26)

We interpret this as being expressed in momentum space, so Δ_o and Δ_1 are approximately diagonal. $\mathcal{V}_A$ is the adiabatic approximation to $\mathcal{V}$.

APPENDIX

Rearrangement Collisions

To supplement the discussion just given we make a few qualitative remarks concerning rearrangement collisions. A more complete account is to be given in Part II.

We consider only the "adiabatic limit" here. The Green's function $(n|W|n')$ for $(H_A + V)$ is then

$$(n|W|n') = \sum_\lambda \frac{\psi_\lambda(n)\psi_\lambda^*(n')}{E - E_\lambda} \qquad . \qquad (A-1)$$

Here, as before, n is an eigenstate of the unperturbed atom; E_λ is the eigenvalue

$$[H_A + V]\psi_\lambda = E_\lambda \psi_\lambda . \qquad (A-2)$$

Now, W satisfies the equation

$$(E - H_A - V) W = 1, \qquad (A-3)$$

where 1 is the unit matrix $\delta_{nn'}$. We next factor W as[21]

$$W = MW_d, \qquad (A-4)$$

where W_d is the diagonal matrix formed from the diagonal elements of W:

$$W_d(n) = \langle n|W|n \rangle . \qquad (A-5)$$

It follows from these equations that the diagonal elements of M are unity:

$$(n|M|n) = 1. \qquad (A-6)$$

We may rewrite Eq. (A-3) as

$$(E - H_A)MW_d = 1 + VMW_d. \qquad (A-7)$$

This is equivalent to

$$(E - H_A - \bar{\mathcal{V}}) MW_d = 1 + (V - \bar{\mathcal{V}})M W_d, \qquad (A-8)$$

where $\bar{\mathcal{V}}$ is a diagonal matrix defined by

$$\bar{\mathcal{V}}(n) \equiv \langle n|VM|n \rangle . \qquad (A-9)$$

Taking the diagonal matrix element of Eq. (A-8) and using (A-9), we find

$$W_d = \frac{1}{E - H_A - \bar{\mathcal{V}}} \qquad (A-10)$$

Similarly, we find from Eq. (A-8)

$$M = \frac{1}{E-H_A-\bar{v}} \frac{1}{W_d} + \frac{1}{E-H_A-\bar{v}}(V-\bar{v})M$$

$$= 1 + \frac{1}{E-H_A-\bar{v}}(V-\bar{v})M$$

$$= 1 + \frac{1}{E-H_A-\bar{v}}PVM_\lambda \qquad\qquad (A-11)$$

(See Eqs. (2-12) and (2-14).)

Thus, we make the identifications $M = F$, $\bar{v} = \mathcal{V}$, and $\frac{1}{d} = W_d$. (A-12)

To apply the above discussion, consider the adiabatic motion of the particle through the atom and suppose the original energy level approaches another — for example, the other might correspond to the pickup of an electron by the charge Q. Label the two unperturbed levels as 0 and 1, and write

$$\mathcal{V}_D \equiv \sum_{\substack{\text{distant} \\ \text{levels}}} \langle 0|V\frac{1}{d}PV|0\rangle .$$

Also, set $\mathcal{V}$ equal to ΔE, the unknown "level shift". Then we have

$$\Delta E = \langle 0|VM|0\rangle \simeq \mathcal{V}(0) + \langle 0|V|1\rangle \frac{1}{d(1)} \langle 1|V|0\rangle \qquad (A-13)$$

and

$$\mathcal{V}(0) \equiv \langle 0|V|0\rangle + \mathcal{V}_D. \qquad\qquad (A-14)$$

Here   d(1) is

$$d(1) \simeq E - W_1 - \mathcal{V}(1)$$
$$= W_o - W_1 + \Delta E - \mathcal{V}(1),$$

where

$$\mathcal{V}(1) = \langle 1|V|1\rangle + \mathcal{V}_D.$$

[Because of the P operator, the states 0 and 1 cannot reoccur in $\mathcal{V}(1)$].
By the use of these expressions Eq. (A-13) becomes

$$\Delta E = \mathcal{V}(0) + \frac{|\langle 1|V|0\rangle|^2}{[W_o - W_1 - \mathcal{V}(1)] + \Delta E} . \qquad (A-15)$$

Solving this equation for $\Delta E \equiv \mathcal{V}$ gives

$$\Delta E_{\pm} = \frac{1}{2} \{ \mathcal{V}(0) + \mathcal{V}(1) + W_1 - W_0 \pm [(\mathcal{V}(0) - \mathcal{V}(1) + W_0 - W_1)^2 + 4| \langle 1|V|0 \rangle |^2]^{\frac{1}{2}} \}.$$

$$(A-16)$$

The resulting energy levels are

$$E_{\pm} = W_0 + \Delta E_{\pm}.$$

$$(A-17)$$

When these lie close together the system may make a nonadiabatic transition between the two levels. The corresponding transition rate has been calculated by Landau,[23] Zener,[24] and Stueckelberg.[25]

The above may be readily generalized to the case that a number of states n correspond to roughly the same value of d. In this case the energy-level shift is

$$\Delta E = \mathcal{V}(0) + \frac{1}{d} [\sum_n' \langle 0|V|n \rangle \langle n|V|0 \rangle].$$

$$(A-18)$$

Here $\sum_n'$ represent a sum over the appropriate states and we have

$$d = -\Delta W + \Delta E - \mathcal{V}(1)$$

$$(A-19)$$

where ΔW is the effective value of $(W_1 - W_0)$. We obtain now an equation of the form (A-16) with $| \langle 1|V|0 \rangle |^2$ replaced by

$$\sum_n' \langle 0|V|n \rangle \langle n|V|0 \rangle .$$

Nonadiabatic transitions may again be calculated using the formulae of Landau, Zener, and Stueckelberg.[23,24,25]

Finally, we consider the case that the original energy level crosses into a continuum. This results, for example, if an outer electron becomes unbound and escapes from the atom.

Let n_f represent such states, say with a free electron. Equation (A-1) tells us that $\frac{1}{d}$ is singular when the crossing occurs. To first order, we identify the states n_f with some of the states λ of Eq. (A-1). Then we have

$$\langle 0|V \frac{1}{d} PV|0 \rangle \simeq \int d\,n_f \frac{\langle 0|V|n_f \rangle \langle n_f|V|0 \rangle}{E - E_{n_f} + i\eta} .$$

This has an imaginary part given by

$$\text{Im}[\mathcal{V}] = -i\pi \int dn_f \ \delta(E - E_{n_f}) \ | \langle n_f | V | 0 \rangle |^2, \qquad \text{(A-20)}$$

which agrees in form with Eq. (3-26).

The above examples show how our formalism may be related to more conventional methods of handling these problems.[26]

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12. Nonrelativistic energies are assumed. This restriction may be easily removed, however.

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15. This is exact in the limit of infinite nuclear mass.

16. We are following the notation of E. Condon and G. Shortly, Theory of Atomic Spectra, (Cambridge University Press, Cambridge 1953) p. 335.

17. Rearrangement collisions are discussed further in the Appendix.

18. Ruby M. Sternheimer, Phys. Rev. $\underline{96}$, 951 (1954).

19. The fact that the $1/x$ behavior in $\mathcal{V}_1$ cancels is due to the accident that the atom is neutral. An ion would of course contribute a $\frac{1}{x}$ term to $\mathcal{V}_1$.

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