Racah, G. (1942), *Phys. Rev.* **62**, 438.
Racah, G. (1943). *Phys. Rev.* **63**, 367.
Racah, G. (1949). *Phys. Rev.* **76**, 1352.
Racah, G. (1951). "Group Theory and Spectroscopy," Lecture Notes, Princeton Univ., Princeton, New Jersey. [*Ergebnisse der Exakten Naturwissenschaften* **37**, 28 (1965).]
Racah, G. (1952). *Phys. Rev.* **85**, 381.
Shi Sheng-Ming (1965). *Chin. Math.* **6**, 610 (Amer. Math. Soc. Trans. of *Acta Math. Sinica*, Peking).
Shudeman, C. L. B. (1937). *J. Franklin Inst.* **224**, 501.
Slater, J. C. (1960). "Quantum Theory of Atomic Structure," Vol. II. McGraw-Hill, New York.
Smith, P. R., and Wybourne, B. G. (1967). *J. Math. Phys.* **8**, 2434.
Smith, P. R., and Wybourne, B. G. (1968), *J. Math. Phys.* **9**, 1040.
Tan Wei-Han, Pi Wu-Chi, Tse Ting-Ting, Nieh Shun-Chuen, Shu Ping-Huo, Tsuei Chen-Chia, Chao Chen-Chou, Li Yung-Hwa, Tong Pong-Fu, and Fong Kuei-Chun (1966). *Chin. J. Phys.* **22**, 38 (Amer. Inst. Phys. Trans. of *Acta Physica Sinica*, Peking).
Trees, R. E. (1951a). *Phys. Rev.* **82**, 683.
Trees, R. E. (1951b). *Phys. Rev.* **83**, 756.
Trees, R. E. (1952). *Phys. Rev.* **85**, 382.
Weyl, H. (1928). "Gruppentheorie und Quantenmechanik." Hirzel, Leipzig. [Transl. by Robertson, H. P. (1931). "The Theory of Groups and Quantum Mechanics." Dover, New York.]
Wybourne, B. G. (1970). "Symmetry Principles in Atomic Spectroscopy." Wiley, New York.

GREEN'S FUNCTION TECHNIQUE IN ATOMIC AND MOLECULAR PHYSICS

GY. CSANAK[1] *and H. S. TAYLOR*[1,2]

Department of Chemistry, University of Southern California
Los Angeles, California

and

ROBERT YARIS[2,3]

Department of Chemistry, Washington University
St. Louis, Missouri

[1] Work partially supported by the National Science Foundation under Grant No. GP-7861.
[2] Alfred P. Sloan Foundation Fellow.
[3] Work partially supported by the National Science Foundation under Grant No. GP-9549, and partially by the Petroleum Research Fund of the American Chemical Society under Grant No. 4341-AC5.

I. Introduction

The purpose of this review is to familiarize the quantum chemist and molecular physicist with some of the ways one can apply the *Green's function technique* to the problems of calculating excitation energies, ionization energies, ground state energies, transition matrix elements, electron absorption coefficients, frequency dependent polarizabilities for atomic and molecular systems, as well as electron–atom, electron–molecule elastic and inelastic scattering cross sections. The Green's function technique was originally defined and applied in quantum field theory (Feynman, 1948; Schwinger, 1951)[4] and extensively used in many-body physics (Galitski and Migdal, 1958) statistical mechanics (Matsubara, 1955; Martin and Schwinger, 1959) and nuclear physics (Migdal, 1967). The sources in these latter fields are difficult for the non-initiated to read since there are different physical conditions, spatial homogeneities, terminologies, etc., which do not apply in atomic and molecular physics. Another form of the field-theoretic or many-body method, the diagrammatic perturbation theory, has been used effectively in the last several years for atomic systems by Kelly (1968) for ground state energies, and by Kelly (1969), Dutta *et al.* (1969) for frequency dependent polarizabilities. There are also early attempts at using Green's functions in quantum chemistry by Linderberg (1968), Reinhardt and Doll (1969), Hedin *et al.* (1969); and in atomic scattering theory by Schneider *et al.* (1970), Janev *et al.* (1969), and Csanak *et al.* (1971). As will be seen, the advantages of this technique are:

(a) *Nonperturbative, self-consistent approximations* (i.e., schemes similar to the Hartree–Fock self-consistent theory) can be developed which go well beyond the Hartree–Fock; e.g., a self-consistent theory of electron scattering cross section and the linear response (Schneider *et al.*, 1970) which leads to self-consistent excitation energies and transition probabilities.

(b) The formalism works *directly in terms of densities, transition amplitudes*, and other quantities (e.g., linear response function) that are measurable,

[4] J. Schwinger (1951) has defined the many particle Green's function (called renormalized —or real—or full Green's function). The free particle Green's function or propagator has been introduced by R. P. Feynman (1948, 1950). For further application, see any book on field theory, e.g., S. S. Schweber: *An Introduction to Relativistic Quantum Field Theory*, Row Peterson and Co., Illinois (1960).

and not in terms of wave functions. This is a great advantage of the Green's function technique. These new functions lend themselves to known approximations that can now be more generally applied. For example, in the calculation of linear response functions (called also frequency dependent polarizabilities), coupled, time-dependent methods are known to be useful (Dalgarno and Victor, 1966; Jamieson, 1969). It will be seen here how such coupled time-dependent methods can be applied to the variety of problems listed in the first paragraph.

(c) *Density matrices and natural orbitals can be calculated directly without prior calculation of the wave functions* (Reinhardt and Doll, 1969) and therefore the Green's function technique is closely related to the density matrix methods already developed in quantum chemistry.

(d) *The optical potential* (the effective one particle scattering potential) can be calculated using the experience gained in coupled time-dependent problems (Schneider *et al.*, 1970).

(e) *Self-consistent perturbation theories* can easily be formulated (i.e., we expand the optical potential in terms of the "real" Green's function, then we choose a trial value for it and calculate an improved "real" Green's function from the Dyson equation, which we substitute back to the perturbation series for the optical potential until self-consistency is achieved) and the derivation of the random phase approximation (R.P.A.) (Ehrenreich and Cohen, 1959; Thouless, 1961; Brout and Carruthers, 1963; Pines, 1961) (called also time-dependent Hartree–Fock theory) can be placed into the context of a hierarchy of approximations (Schneider *et al.*, 1970). These approximations, in turn, can be made self-consistent at each truncation. As in simple Hartree–Fock theory, self-consistency will be seen to be a physically desirable feature of the approximation method. As will become evident, this review is formal, in that there exist at this time no self-consistent results.

It is hoped that this exposition will encourage quantum chemists and molecular physicists with practical calculational experience to put the formalism to the test. The authors of this review believe the formalism is as practical as present-day configuration interaction, perturbation, close coupled and adiabatic methods that are presently being used. It is hoped that self-consistency will yield better results for equal effort.

In Section II we shall introduce the formalism of second quantization, define the many-particle Green's functions and outline some elementary properties of the one- and two-particle Green's functions. It will be shown how physical information can be obtained from a knowledge of these functions. In Section III the hierarchy of equations for the Green's functions is derived. As important are alternative forms of these hierarchies in terms of the spectral functions for the Green's functions and in terms of optical (effective) one-, two-, and many-particle potentials. In Section IV the expressions

for scattering cross sections are derived. In Sections V and VI, respectively, nonperturbative and perturbative self-consistent methods of solving for the Green's function are given. It is in Sections V and VI that physical intuition comes into play.

Throughout this review a familiarity with the methods of second quantization as well as the use of the Heisenberg and interaction representation will be assumed.[5]

II. Many-Particle Green's Functions and Physical Quantities[6]

A. The Many-Particle Green's Function—Physical Quantities and the One-Particle Green's Function

The general n-particle Green's function (also called real or full or renormalized Green's function) is defined as

$$G_n(1, 2, \ldots, n; 1', 2', \ldots, n') = (i)^{-n}\langle\Psi_0|T[\psi(1)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]|\Psi_0\rangle. \tag{1}$$

Here, $i = \mathbf{r}_i, t_i$;[7] $|\Psi_0\rangle$ is the ground-state of an N-particle system; $\psi(i)$ *is the field operator* in the Heisenberg representation, i.e., the operator which destroys an electron at position $\mathbf{r}_i$ at time t_i; $\psi^\dagger(i)$ is the analogous "creation" operator. As always in the Heisenberg representation, the operators are time dependent even when the corresponding operator is time independent in the Schroedinger representation, since

$$\begin{aligned} Op(i)_{\text{Heisenberg}} &= e^{iHt_i}Op(\mathbf{r}_i, 0)e^{-iHt_i} \\ &= e^{iHt_i}Op(\mathbf{r}_i)_{\text{Schroedinger}}e^{-iHt_i}. \end{aligned} \tag{2}$$

Here H is the Hamiltonian of the total system and $\hbar$ is set equal to 1. It is well to remember that antisymmetry is automatically built into the second quantized formalism since all operators are written in terms of ψ and $\psi^\dagger$ (e.g., the potential is written as

$$V = \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi^\dagger(\mathbf{r}_1)\psi^\dagger(\mathbf{r}_2)V(|\mathbf{r}_1 - \mathbf{r}_2|)\psi(\mathbf{r}_2)\psi(\mathbf{r}_1)$$

[5] For elementary introduction to second quantization and many-body theory, see, e.g., Falkoff (1962), Roman (1965), Kirzhnits (1967), March *et al.* (1967) and Mattuck (1967).

[6] Matsubara (1955), Galitski and Migdal (1958), Martin and Schwinger (1959), Falkoff (1962), Roman (1965), Kirzhnits (1967), March *et al.* (1967), Mattuck (1967), and Migdal (1967).

[7] $i = 1, 2, \ldots, n$. $\mathbf{r}_i$ means position and spin coordinate. Any integration for $\mathbf{r}$ means integration in position space and summation in spin space.

in the Schroedinger representation, and as

$$V(t) = \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi^\dagger(\mathbf{r}_1 t)\psi^\dagger(\mathbf{r}_2 t)V(|\mathbf{r}_1 - \mathbf{r}_2|)\psi(\mathbf{r}_2 t)\psi(\mathbf{r}_1 t) \tag{3}$$

in the Heisenberg representation) and these in turn satisfy for equal times the anticommutation rules for Fermi–Dirac particles

$$\begin{aligned} [\psi(\mathbf{r}t), \psi(\mathbf{r}'t)]_+ &= [\psi^\dagger(\mathbf{r}t), \psi^\dagger(\mathbf{r}'t)]_+ = 0 \\ [\psi(\mathbf{r}t), \psi^\dagger(\mathbf{r}'t)]_+ &= \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \tag{4}$$

The symbol T in Eq. (1) is the Wick time-ordering operator, which, when applied to a product of operators, arranges them in chronological order of their time arguments with a multiplicative factor of ± 1 depending on whether the chronological order is an even or odd permutation of the original order.

As an example note

$$\begin{aligned} T[\psi(1)\psi^\dagger(1')] = {} & \psi(1)\psi^\dagger(1')\Theta(t_1 - t_1') \\ & - \psi^\dagger(1')\psi(1)\Theta(t_1' - t_1) \end{aligned} \tag{5}$$

where Θ is the Heaviside (unit step) function, hence

$$\begin{aligned} G_1(1, 1') = (i)^{-1}\{&\Theta(t_1 - t_1')\langle\psi(1)\psi^\dagger(1')\rangle \\ & - \Theta(t_1' - t_1)\langle\psi^\dagger(1')\psi(1)\rangle\}. \end{aligned} \tag{6}[8]$$

From this formula flows a simple interpretation of the one-particle Green's function. If $t_1' < t_1$ then

$$\begin{aligned} G(1, 1') &= (1/i)\,\langle\psi(1)\psi^\dagger(1')\rangle \\ &= (1/i)\, e^{iE_0(t_1 - t_1')}\langle\Psi_0|\psi(\mathbf{r}_1)e^{-iH(t_1 - t_1')}\psi^\dagger(\mathbf{r}_1')|\Psi_0\rangle \end{aligned}$$

Now, $\psi^\dagger(\mathbf{r}_1')|\Psi_0\rangle$ represents a state where a particle was created at position $\mathbf{r}_1'$ in the background of the N-particle ground-state and

$$e^{-iH(t_1 - t_1')}\psi^\dagger(\mathbf{r}_1')|\Psi_0\rangle$$

represents the state which was formed from the previous one (assuming it was created at time t_1') from time t_1' to time t_1. The second factor in the previous expression therefore represents the scalar product of this state with the state $\psi^\dagger(\mathbf{r}_1)|\Psi_0\rangle$ which is an extra particle at point $\mathbf{r}_1$ with the ground-state background of N particles. The first factor is a phase factor. Therefore $G(1, 1')$ for $t_1' < t_1$ is the probability amplitude that if an extra particle is

[8] Where it will not cause confusion we shall usually use angular brackets to denote an expectation value with respect to $|\Psi_0\rangle$, i.e.,

$$\langle O_p\rangle \equiv \langle\Psi_0|O_p|\Psi_0\rangle$$

created at time t_1' and point $\mathbf{r}_1'$, then it will be found at time t_1 at the point $\mathbf{r}_1$.

$G(1, 1')$ describes the propagation of a particle in an N-particle ground-state, therefore $G(1, 1')$ is also called the "real" or "full" or "renormalized" one-particle propagator, because it describes the actual propagation of an extra particle in the "medium" of the N-particle ground state. For $t_1 < t_1'$ we destroy a particle at point $\mathbf{r}_1$ at time t_1 and then measure that this destruction shows up at time t_1' at the point $\mathbf{r}_1'$. We shall call this process the creation and propagation of a "hole."

We can define the following related functions

$$G^{>}(1, 1') = (1/i)\langle\psi(1)\psi^{\dagger}(1')\rangle$$
$$G^{<}(1, 1') = -(1/i)\langle\psi^{\dagger}(1')\psi(1)\rangle.$$

These are called correlation functions, and

$$G^{R}(1, 1') = (1/i)\Theta(t_1 - t_1')\langle[\psi(1), \psi^{\dagger}(1')]_{+}\rangle$$

the retarded one-particle Green's function

$$G^{A}(1, 1') = -(1/i)\Theta(t_1' - t_1)\langle[\psi^{\dagger}(1')\psi(1)]_{+}\rangle$$

the advanced one-particle Green's function.

Since

$$\begin{aligned}\langle\psi(1)\psi^{\dagger}(1')\rangle &= \langle e^{iHt_1}\psi(\mathbf{r}_1)e^{-iHt_1}e^{iHt_1'}\psi^{\dagger}(\mathbf{r}_1')e^{-iHt_1'}\rangle \\ &= \langle e^{iE_0t_1}\psi(\mathbf{r}_1)e^{-iH(t_1-t_1')}\psi^{\dagger}(\mathbf{r}_1')e^{-iE_0t_1'}\rangle \\ &= \langle\psi(\mathbf{r}_1)e^{-i(H-E_0)\tau}\psi^{\dagger}(\mathbf{r}_1')\rangle \qquad (7)\end{aligned}$$

where $\tau = t_1 - t_1'$, G_1 depends only on τ and can be written as

$$\begin{aligned}G_1(1, 1') &= (i)^{-1}\{\Theta(\tau)\langle\psi(\mathbf{r}_1)e^{-i(H-E_0)\tau}\psi^{\dagger}(\mathbf{r}_1')\rangle \\ &\quad - \Theta(-\tau)\langle\psi^{\dagger}(\mathbf{r}_1')e^{i(H-E_0)\tau}\psi(\mathbf{r}_1)\rangle\} \\ &\equiv G_1(\mathbf{r}_1, \mathbf{r}_1', \tau) \qquad (8)\end{aligned}$$

which expresses time homogeneity for time-independent potentials.

As will be seen later, similar, but more complicated formulas can be written for higher G_n.

To justify going further it will now be demonstrated how a knowledge of G_1 (or $G^{<}$) enables one to calculate the one-particle density matrix of the system (and thus all expectation values of one-particle operators over the ground state Ψ_0) and also the ground-state energy.

The *density operator* $\rho_{op}(\mathbf{r})$, whose expectation value is the density at position $\mathbf{r}$, is given in the Schroedinger representation as

$$\rho_{op}(\mathbf{r}) = \sum_{i=1}^{n}\delta(\mathbf{r} - \mathbf{r}_i) \qquad (9)$$

and in the Heisenberg second quantized form as

$$\begin{aligned}\rho_{op}(\mathbf{r}t) &= \int d\mathbf{r}'\psi^{\dagger}(\mathbf{r}'t)\delta(\mathbf{r} - \mathbf{r}')\psi(\mathbf{r}'t) \\ &= \psi^{\dagger}(\mathbf{r}t)\psi(\mathbf{r}t). \qquad (10)\end{aligned}$$

Therefore, the *density* at position $\mathbf{r}$ and time t is

$$\begin{aligned}\rho(\mathbf{r}t) &= \langle\psi^{\dagger}(\mathbf{r}t)\psi(\mathbf{r}t)\rangle \\ &= \lim_{t-t'\to-0}\langle\psi^{\dagger}(\mathbf{r}t')\psi(\mathbf{r}t)\rangle \qquad (11)\end{aligned}$$

Since in taking the limit, t' approaches t from above (-0 means t' is always larger than t), we can insert T and write[9]

$$\begin{aligned}\rho(\mathbf{r}t) &= \lim_{t-t'\to-0}\langle T[\psi^{\dagger}(\mathbf{r}t')\psi(\mathbf{r}t)]\rangle \\ &= \lim_{t-t'\to-0}\{-\langle T[\psi(\mathbf{r}t)\psi^{\dagger}(\mathbf{r}t')]\rangle\} \\ &= \lim_{\tau\to-0}\{-iG(\mathbf{r}, \mathbf{r}; \tau)\} \qquad (12)\end{aligned}$$

From Equation (11) one could alternatively have written

$$\rho(\mathbf{r}t) = -iG^{<}(\mathbf{r}t, \mathbf{r}t) \qquad (13)$$

and we see that $G^{<}(\mathbf{r}t, \mathbf{r}t)$ gives the density. In practice $G(\tau)$[10] will be determined as its *time Fourier transform* $G(\omega)$ where

$$G(\omega) = \int_{-\infty}^{\infty}d\tau G(\tau)e^{i\omega\tau} \qquad (14a)$$

for any complex ω and the inverse transform

$$G(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\, G(\omega)\, e^{-i\omega\tau}. \qquad (14b)$$

Similarly we can define $G^{<}(\omega)$, $G^{>}(\omega)$ as well as $G^{R}(\omega)$, $G^{A}(\omega)$.

Then Eq. (12) simply means that if $G(\omega)$ is known, then $i\rho(\mathbf{r})$ is determined by integrating this function over a semicircular contour going along the real ω axis from $-\infty$ to $+\infty$ by closing counterclockwise in the upper half plane (uhp). The closure is in the uhp because τ is always negative,

[9] Where it will not cause confusion we shall sometimes drop the superscript 1 on G_1, r_1, t_1, etc. Hence an unsubscripted G, r, t means G_1, r_1, t_1, etc.

[10] Sometimes we waive writing out all coordinates. Here we omitted the space coordinates of G.

hence $e^{-i\omega\tau}$ will only vanish along the semicircle when Im ω is positive. After fixing the path of integration we can take the limit behind the integral sign and we shall get a unit factor instead of the exponential. The sometimes confusing limit in Eq. (12) simply specifies a contour. Clearly the density is now known if $G(\tau)$ or $G^<(\tau)$ or $G(\omega)$, or the poles and residues of $G(\omega)$ are known in the uhp. In the practical problems which we are concerned with in this review, the residues and poles of $G(\omega)$ shall be solved for and used to obtain the density. Such being the case, the so-called spectral representation of $G(\omega)$, which shows explicitly its poles and branchcuts, residues and discontinuities along the branchcuts, will soon be discussed.

If for some reason the poles are more difficult to obtain than an expression for $G(\omega)$, $\rho(\mathbf{r})$ and (as we shall see shortly) E_0, *the ground state energy* can be evaluated by integrating over the contour directly. This is accomplished most easily by rotating the contour counterclockwise by $\pi/2$. The spectral representation will show that the rotated contour encloses the same poles as the original one. On the infinite semicircle in the left half plane the form of $G(\omega)$ will be obvious from the spectral representation and the integral can be performed analytically. On the part along the imaginary axis one can integrate numerically (there are no singularities along the imaginary ω axis) moving symmetrically (up and down) from the real axis until $G(\omega)$ reaches its large ω asymptotic form, at which point analytic integration again can be used.

It will now be shown that the same residues and poles also determine the ground state energy. In this demonstration *the equation of motion for* $\psi(1)$, to be derived in the next section must be used. This equation is

$$\left[i\frac{\partial}{\partial t} - h(\mathbf{r})\right]\psi(\mathbf{r}t) = \int d\mathbf{r}' V(\mathbf{r}-\mathbf{r}')\psi^\dagger(\mathbf{r}'t)\psi(\mathbf{r}'t)\psi(\mathbf{r}t) \tag{15}$$

where h is the one-particle part of the Hamiltonian and V is the two-particle potential. The key to obtaining the energy is to evaluate the derivative of $G(\mathbf{r}t;\mathbf{r}'t')$ with respect to t in the special case of $t < t' = 0$ which specifies the time ordering, viz.

$$\begin{aligned}[\partial G(\mathbf{r}t;\mathbf{r}'0)/\partial t]_{t<0} &= i\langle\psi^\dagger(\mathbf{r}'0)\,\partial/\partial t\psi(\mathbf{r}t)\rangle \\ &= \langle\psi^\dagger(\mathbf{r}'0)\int d\mathbf{r}'' V(\mathbf{r}-\mathbf{r}'')\psi^\dagger(\mathbf{r}''t)\psi(\mathbf{r}''t)\psi(\mathbf{r}t)\rangle \\ &\quad + \langle\psi^\dagger(\mathbf{r}'0)h(\mathbf{r})\psi(\mathbf{r}t)\rangle. \end{aligned} \tag{16}$$

Using the right-hand side of (16), the following limit can be taken

$$\lim_{\substack{\mathbf{r}'\to\mathbf{r}\\ t\to -0}} \frac{\partial G(\mathbf{r}t;\mathbf{r}'0)}{\partial t}. \tag{17}$$

A comparison of (16) with the second quantized expressions for $\langle H_0\rangle$ and $\langle V\rangle$ gives the value of the limit in (17) after integration for $\mathbf{r}$ as $\langle H_0\rangle + 2\langle V\rangle$. Since $E_0 = \langle H_0\rangle + \langle V\rangle$ one obtains

$$E_0 = \frac{1}{2}\left\{\int d\mathbf{r} \lim_{\substack{\mathbf{r}'\to\mathbf{r}\\ \tau\to -0}} \frac{\partial G(\mathbf{r},\mathbf{r}';\tau)}{\partial\tau} + \langle H_0\rangle\right\} \tag{18}$$

From Eq. (12) the second term on the right-hand side is

$$\langle H_0\rangle = -i\int d\mathbf{r} \lim_{\substack{\tau\to -0\\ \mathbf{r}'\to\mathbf{r}}} h(\mathbf{r})G(\mathbf{r},\mathbf{r}';\tau)$$

hence *the ground-state energy*:

$$\begin{aligned} E_0 &= \frac{1}{2}\int d\mathbf{r} \lim_{\substack{\tau\to -0\\ \mathbf{r}'\to\mathbf{r}}}\left[\frac{\partial}{\partial\tau} - ih(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';\tau) \\ &= -\frac{i}{4\pi}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r} \lim_{\mathbf{r}'\to\mathbf{r}} [\omega + h(\mathbf{r})]G(\mathbf{r},\mathbf{r}';\omega) \end{aligned} \tag{19}$$

Again the limit $\tau\to -0$ simply means that one must close the contour in the ω plane in the uhp, and also the knowledge of the spectral representation of $G(\omega)$ will allow the calculation of E_0. Note that both E_0 and ρ depend only on $G^<(\tau)$.

From the interpretation of the one-particle Green's function it is obvious that G_1 will be related to the elastic scattering cross section (Bell and Squires, 1959; Kato *et al.*, 1960; Namiki, 1960). Though the formula for the cross section is simple, the explanation is not straightforward and we should refer to the adiabatic principle and the formulation of field theory in the Heisenberg representation (Roman, 1965). We shall give only a simplified schematic description.

The *elastic scattering cross-section* in the Green's function formalism was first formulated by Bell and Squires (1959) and by Namiki (1960). One can formally simplify the calculation using the so-called in-out or LSZ reduction formalism (Falkoff, 1962; Roman, 1965; Kirzhnits, 1967; March *et al.*, 1967) in which adiabatic decoupling is applied to the operators.

Let us denote by $\psi(\mathbf{r}t)$ the electron field operator and by $|\Psi_0\rangle$ the ground state of the target (Roman, 1965). It can be shown that as $t\to\mp\infty$ with simultaneous adiabatic decoupling of the electron–atom interaction the field operator will converge to an asymptotic form which obeys the free equation of motion (Roman, 1965). Therefore,

$$\lim_{t\to\mp\infty}\psi(\mathbf{r}t) = \lim_{t\to\mp\infty}\psi^{\text{out}}(\mathbf{r}t) = \lim_{t\to\mp\infty}\psi^{\text{free}}(\mathbf{r}t) \tag{20a}$$

where $\psi^{in}(\mathbf{r}t)$ and $\psi^{out}(\mathbf{r}t)$ is the asymptotic form of $\psi(\mathbf{r}t)$ in the distant past and distant future. It is stressed that the adiabatic decoupling considered here refers to the electron–atom interaction. This process can be handled in a nontrivial manner in the field theoretic formalism. See, for example, Klein (1956) and Klein and Zemach (1957). $\psi^{in}(\mathbf{r}t)$ and $\psi^{out}(\mathbf{r}t)$ can be expanded in terms of propagating plane waves $\varphi_{\mathbf{k}}(\mathbf{r}t)$ of momentum $\mathbf{k}$:

$$\psi^{out}(\mathbf{r}t) = \sum_{\mathbf{k}} a_{\mathbf{k}}^{out} \varphi_{\mathbf{k}}(\mathbf{r}t) \tag{20b}$$

This defines $a_{\mathbf{k}}^{out}$. Now, the scattering state corresponding to an $\{^{\text{incoming}}_{\text{outgoing}}\}$ electron of momentum $\mathbf{k}$ can be written as

$$|\Psi_{\mathbf{k}}^{\pm}\rangle = a_{\mathbf{k}}^{\dagger out}|\Psi_0\rangle \tag{21}$$

and from Eq. (20a) and (20b)

$$a_{\mathbf{k}}^{\dagger out} = \lim_{t \to \mp\infty} a_{\mathbf{k}}^{\dagger}(t) \tag{20c}$$

where $a_{\mathbf{k}}(t)$ is the expansion coefficient appearing in the expansion of $\psi(\mathbf{r}t)$

$$\psi(\mathbf{r}t) = \sum_{\mathbf{k}} a_{\mathbf{k}}(t)\varphi_{\mathbf{k}}(\mathbf{r}t). \tag{20d}$$

Basically, Eq. (21) says that the scattering functions $|\Psi_{\mathbf{k}}^{\pm}\rangle$ are those that connect adiabatically, when the electron–atom interaction is turned off infinitesimally slowly, to the state in which a free electron moving "in" toward or "out" from the target is created in the field of the ground state. This, of course, is an idealization of the experimental situation. The $|\Psi_{\mathbf{k}}^{\pm}\rangle$ of Eq. (21) can be shown to satisfy the Lippman–Schwinger equation for electron–atom scattering (Bell and Squires, 1959; Namiki, 1960). (See also Klein, 1956; Klein and Zemach, 1957; Fetter and Watson, 1965.) The scattering matrix can be written

$$\begin{aligned} S_{\mathbf{k}'\mathbf{k}} &= \langle \Psi_{\mathbf{k}'}^{-} | \Psi_{\mathbf{k}}^{+} \rangle = \langle \Psi_0 | a_{\mathbf{k}'}^{out} a_{\mathbf{k}}^{\dagger in} | \Psi_0 \rangle \\ &= \lim_{\substack{t' \to \infty \\ t \to -\infty}} \langle \Psi_0 | a_{\mathbf{k}'}(t') a_{\mathbf{k}}^{\dagger}(t) | \Psi_0 \rangle \\ &= \lim_{\substack{t \to -\infty \\ t' \to +\infty}} \langle \Psi_0 | a_{\mathbf{k}'}(t') a_{\mathbf{k}}^{\dagger}(t) | \Psi_0 \rangle \\ &= \lim_{\substack{t \to -\infty \\ t' \to +\infty}} \int d\mathbf{r}\, d\mathbf{r}' \varphi_{\mathbf{k}'}^{*}(\mathbf{r}'t') \langle \Psi_0 | \psi(\mathbf{r}'t') \psi^{\dagger}(\mathbf{r}t) | \Psi_0 \rangle \varphi_{\mathbf{k}}(\mathbf{r}t) \\ &= i \lim_{\substack{t \to -\infty \\ t' \to +\infty}} \int d\mathbf{r}'\, d\mathbf{r} \varphi_{\mathbf{k}'}^{*}(\mathbf{r}'t') G(\mathbf{r}'t', \mathbf{r}t) \varphi_{\mathbf{k}}(\mathbf{r}t). \end{aligned} \tag{22}$$

Note that since G contains only $|\Psi_0\rangle$, as opposed to $|\Psi_n\rangle$ $(n \neq 0)$, it alone cannot supply inelastic scattering information. Equation (22) shows clearly how elastic scattering is related to a knowledge of G.

A knowledge of G can be shown to give the *natural orbitals* and the *ionization potential* of the bound electrons of the target. The former statement is fairly obvious at this point, since a slight generalization of (12) shows that G gives the density matrix, and natural orbitals are those functions which diagonalize this matrix. Its general matrix element is

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') &= N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi_0^{*}(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi_0(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N) \\ &= \langle \psi^{\dagger}(\mathbf{r}) \psi(\mathbf{r}') \rangle \end{aligned}$$

or

$$\rho(\mathbf{r}, \mathbf{r}') = -i \lim_{\tau \to -0} G(\mathbf{r}, \mathbf{r}'; \tau) = -iG^{<}(1^{+}, 1'). \tag{23}$$

The density matrix, since it is diagonal in the natural orbitals $\chi_i(\mathbf{r})$, can also be written as (Löwdin, 1955)

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i n_i \chi_i(\mathbf{r}) \chi_i^{*}(\mathbf{r}') \tag{24}$$

where n_i are the occupation numbers. The $\chi_i(\mathbf{r})$ are orthonormal as $\rho(\mathbf{r}, \mathbf{r}')$ is an Hermitian matrix. The Green's function method is clearly the way to calculate the density matrix and the natural orbitals directly. It might seem somewhat redundant to obtain natural orbitals once G_1 is known and E_0 can be calculated. This is really a question of practicality in that it has been shown that it is easier to calculate good approximate natural orbitals than $\rho(\mathbf{r}, \mathbf{r}')$ in that the occupation numbers in the method of Reinhardt and Doll (1969) are poor. It is then suggested that E_0 be calculated variationally with the natural orbitals as the basis set. Since the iterative methods, to be discussed later, were not tried by Reinhardt and Doll (1969), it is hoped that by using them a direct calculation of E_0 using Eq. (19) will be more successful.

To further illuminate the relationship between the natural orbitals, the ionization energies and the density matrix it is well to write what is known as *the spectral representation of* G_1 (mentioned earlier in this section). Starting with Eq. (6) and inserting a complete set of $N+1$ and $N-1$ particle state functions in the first and second terms on the left-hand side, respectively gives

$$\begin{aligned} G_1(1, 1') = (1/i)\Big\{ &\Theta(t_1 - t_1') \sum_n \langle \Psi_0^{N} | \psi(1) | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | \psi^{\dagger}(1') | \Psi_0^{N} \rangle \\ &- \Theta(t_1' - t_1) \sum_m \langle \Psi_0^{N} | \psi^{\dagger}(1') | \Psi_m^{N-1} \rangle \langle \Psi_m^{N-1} | \psi(1) | \Psi_0^{N} \rangle \Big\}. \end{aligned} \tag{25}$$

The superscript now denotes the number of particles. Introducing the "orbital" definitions, called *Feynman–Dyson amplitudes*

$$f_n(1) = \langle \Psi_0 | \psi(1) | \Psi_n^{N+1} \rangle = \langle \Psi_0 | \psi(\mathbf{r}_1) | \Psi_n^{N+1} \rangle \exp[-i(E_n^{N+1} - E_0^N)t_1]$$
$$\equiv f_n(\mathbf{r}_1) \exp[-i(E_n^{N+1} - E_0^N)t_1] \tag{26a}$$

$$g_n(1) = \langle \Psi_n^{N-1} | \psi(1) | \Psi_0^N \rangle = \langle \Psi_n^{N-1} | \psi(\mathbf{r}_1) | \Psi_0^N \rangle \exp[i(E_n^{N-1} - E_0^N)t_1]$$
$$\equiv g_n(\mathbf{r}_1) \exp[i(E_n^{N-1} - E_0^N)t]. \tag{26b}$$

Equation (25) becomes in terms of the f and g orbitals

$$G(1, 1') = -i\Big\{\Theta(\tau) \sum_n f_n(1) f_n^*(1') - \Theta(-\tau) \sum_m g_m^*(1') g_m(1)\Big\}$$
$$= -i\Big\{\Theta(\tau) \sum_n f_n(\mathbf{r}) f_n^*(\mathbf{r}') \exp[-i(E_n^{N+1} - E_0^N)\tau]$$
$$- \Theta(-\tau) \sum_m g_m(\mathbf{r}) g_m^*(\mathbf{r}') \exp[-i(E_0^N - E_m^{N-1})\tau]\Big\} \tag{27}$$

From a comparison of (23), (24), and (27), it is tempting to equate the one-hole ($N \leftrightarrow N-1$) Feynman amplitudes with the natural orbitals, because we obtain

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_m g_m(\mathbf{r}') g_m^*(\mathbf{r}) \tag{28a}$$

Unfortunately, the g's are not orthogonal, nor even linearly independent. The f's, the one-particle ($N \leftrightarrow N+1$) Feynman amplitudes are also not linearly independent. In fact the only thing that can generally be proved about f and g is the completeness of the total set

$$\sum_n f_n(\mathbf{r}) f_n^*(\mathbf{r}') + \sum_m g_m(\mathbf{r}) g_m^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{28b}$$

Goscinski and Linder (1970) have shown how to use Löwdin's (1956) method of canonical orthogonalization to transform the g's into the χ's. This procedure shall not be reviewed here since it is readily available in the original reference and is clearly readable to quantum chemists.

The ionization energies and electron attachment energies to various states of the $N-1$ and $N+1$ particle system clearly appear in Eq. (27).

To see how the ionization energies are poles of G_1, Eq. (27) is Fourier transformed using

$$\int_{-\infty}^{\infty} dt[\Theta(t)e^{-i\alpha t}]e^{i\omega t} = \lim_{\eta \to +0} \frac{i}{\omega - \alpha + i\eta} \tag{29a}$$

or

$$\Theta(t) = -\frac{1}{2\pi i} \lim_{\eta \to +0} \int_{-\infty}^{\infty} d\omega \frac{1}{\omega + i\eta} e^{-i\omega t}. \tag{29b}$$

The former formula is easily verified by performing an inverse transform of the right-hand side, i.e., multiply by $e^{-i\omega t}/2\pi$ and integrate from $\omega = -\alpha$ by completing the contour. For $t < 0$ the contour must be closed in the uhp resulting in a zero value for the integral. For $t > 0$ the contour must be closed in the lhp and a single pole at $\alpha - i\eta$, gives a residue which in the limit is $e^{-i\alpha t}$. Similarly,

$$\int_{-\infty}^{\infty} dt[\Theta(-t)e^{-i\alpha t}]e^{i\omega t} = \lim_{\eta \to +0} \frac{-i}{\omega - \alpha - i\eta}. \tag{30}$$

With this the Fourier transform of Eq. (27) is obtained using (14), i.e.,

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \to +0} \Big[\sum_n \frac{f_n(\mathbf{r}) f_n^*(\mathbf{r}')}{\omega - (E_n^{N+1} - E_0^N) + i\eta} + \sum_m \frac{g_m(\mathbf{r}) g_m^*(\mathbf{r}')}{\omega - (E_0^N - E_m^{N-1}) - i\eta}\Big] \tag{31}$$

Clearly, in the limit, the poles of the second term are at the ionization energies which can take on both discrete and continuous values. One discrete value occurs for each bound state of the $N-1$ particle system. For a neutral N electron system the physical poles of the second term appear in the second quadrant of the complex plane and fall on a line $\omega = i\eta$, $\eta > 0$, i.e., infinitesimally above the real axis. They are discrete for small negative real ω, and merge into a branch cut for a larger negative ω. The physical poles of the first term of (31) all lie in the lhp along a line $\omega = -i\eta$, $\eta > 0$. If there exist bound states of the negative ion discrete poles appear in the third quadrant. A cut always appears along this line in the fourth quadrant. The situation is schematized on Fig. 1.

These analytic properties will be useful later when $G(\omega)$ is found by solving for its spectrum. A knowledge of where these singularities lie narrows the region of the complex plane to be searched. Clearly our arguments must be modified if N does not represent a neutral system. The reader should also be reminded that if the definition of $G(\omega)$ which is essentially given for real ω, is extended into the whole complex plane, then the mentioned poles and branch cuts arise. Because $G(\omega)$ has branch cuts on a part of the real axis we can define by analytic continuation a function on the double-sheet complex plane which has no branch cut. By this analytic continuation new poles will appear on the unphysical sheets which are reached when the path of continuation crosses the above-mentioned physical cuts. This shall be discussed more fully in the next section where the poles and residues are sought. One can prove that $G(\omega)$ coincides with $G^A(\omega)$ below the left-hand branch cut

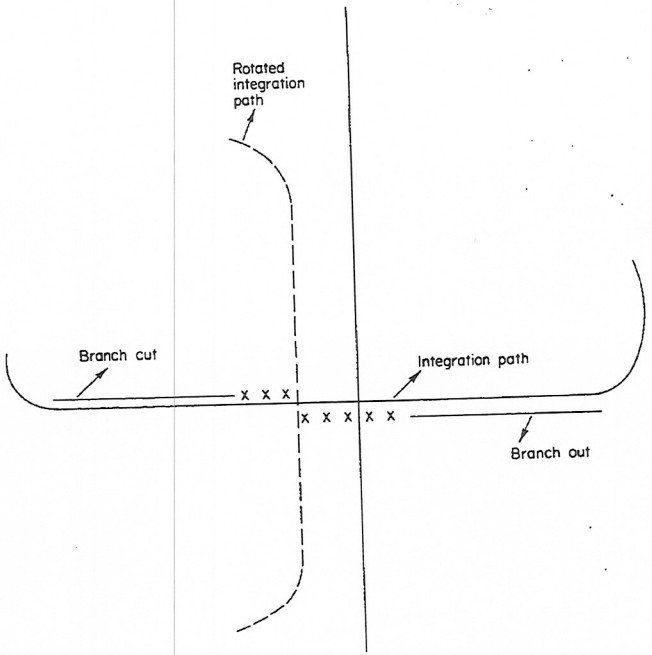


FIG. 1. Poles and branch cuts of $G(\omega)$.

and $G^A(\omega)$ is the analytic continuation of $G(\omega)$ above this branch cut and $G(\omega)$ coincides with $G^R(\omega)$ above the right-hand branch cut and $G^R(\omega)$ is the analytic continuation of $G(\omega)$ into the lower half plane across this cut. $G^R(\omega)$ is regular in the upper half plane whereas $G^A(\omega)$ is regular in the lower half plane. It will be seen that the ability to use finite discrete basis sets greatly simplifies this problem.

B. The Two-Particle Green's Function

It is now useful to turn to a discussion of G_2. In G_2 four times appear and as might be expected from the discussion of G_1, different specific time orderings yield different information. An equation analogous to Eq. (6) could be written but each term would now require three Heaviside functions (four times three relative times). Fortunately for the purpose of this review, which is concerned with excitation energies and inelastic scattering of electrons from atomic and molecular targets, only a few specific time orderings shall be necessary to obtain such information. To illustrate this, several time orderings shall be considered.

Case I. Set $t_1, t_1' > t_2, t_2'$ for arbitrary order of t_1 and t_1' and for arbitrary order of t_2 and t_2'. Then for this case

$$\begin{aligned} G_2(1,2;1',2')^{\mathrm{I}} &= (i)^{-2}\langle \Psi_0^N | T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')] | \Psi_0^N\rangle \\ &= -\langle \Psi_0^N | T[\psi(1)\psi^\dagger(1')]T[\psi(2)\psi^\dagger(2')] | \Psi_0^N\rangle \\ &= -\sum_n \langle \Psi_0^N | T[\psi(1)\psi^\dagger(1')] | \Psi_n^N\rangle\langle \Psi_n^N | T[\psi(2)\psi^\dagger(2')] | \Psi_0^N\rangle \\ &= -\sum \langle \Psi_0^N | T[\psi(1)\psi^\dagger(1')] | \Psi_n^N\rangle\langle \Psi_n^N | T[\psi(2)\psi^\dagger(2')] | \Psi_0^N\rangle \\ &= -\sum_n \chi_n(1,1')\tilde{\chi}_n(2,2'). \end{aligned} \tag{32}$$

Here an N particle-state closure has been inserted and the *hole-particle (Bethe–Salpeter) amplitudes* have been defined as

$$\begin{aligned} \chi_n(1,1') &= \langle \Psi_0^N | T[\psi(1)\psi^\dagger(1')] | \Psi_n^N\rangle \\ \tilde{\chi}_n(1,1') &= \langle \Psi_n^N | T[\psi(1)\psi^\dagger(1')] | \Psi_0^N\rangle. \end{aligned} \tag{33}$$

It is well to note that it was the specific time ordering that resulted in two hole-particle products, i.e., the pairing of creation and annihilation operators. Other time orderings will give other pairings such as hole–hole and particle–particle. This point is important because only for hole–particle pairings do the intermediate states have to be N-particle states; it shall be seen that this results in poles related to the excitation energies of the N-particle system and not intermediate states representing double positive and negative ion states with poles representing double ionization and affinity energies, respectively. To see this explicitly, it is well to write out the right-hand side of Eq. (33) in detail using the Heaviside functions for the time of two time orderings and making the times explicit by using Eq. (2). If this is done, after some algebra the following result is obtained

$$\chi_n(1,1') = \exp\,[(i/2)(E_0^N - E_n^N)(t_1 + t_1')]\chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1) \tag{34}$$

where

$$\begin{aligned} \chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1) = {} & \Theta(\tau_1)\exp\,[i(E_0^N + E_n^N)\tau_1/2] \\ & \times \langle \Psi_0^N | \psi(\mathbf{r}_1) e^{-iH\tau_1}\psi^\dagger(\mathbf{r}_1') | \Psi_n^N\rangle \\ & - \Theta(-\tau_1)\exp\,[-i(E_0^N + E_n^N)\tau_1/2] \\ & \times \langle \Psi_0 | \psi^\dagger(\mathbf{r}_1') e^{iH\tau_1}\psi(\mathbf{r}_1) | \Psi_n^N\rangle \end{aligned} \tag{35}$$

Using Eq. (32), this gives

$$G_2(1,2;1',2')^{\mathrm{I}} = -\sum_{n=0}^{\infty} \exp\,[i(E_0^N - E_n^N)\tau]\chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)\tilde{\chi}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \tag{36}$$

for $t_1, t_1' > t_2, t_2'$ but arbitrary τ_1, τ_2. Here the following changes to relative time variables have been introduced.

$$\tau = \tfrac{1}{2}(t_1 + t_1') - \tfrac{1}{2}(t_2 + t_2') \qquad \tau_i = t_i - t_i' \qquad (i = 1, 2).$$

The important point is that (36) has three relative times, the exponential argument of one of them being simultaneously completely factorable from the matrix elements and being an excitation energy. The only other time ordering giving this property is the other hole–particle case, $t_2, t_2' > t_1, t_1'$. The result here is:

Case II.

$$G_2(1, 2; 1', 2')^{\mathrm{II}} = -\sum_{n=0}^{\infty} \exp\,[-i(E_0^N - E_n^N)\tau]\tilde{\chi}_n(\tau_1)\chi_n(\tau_2). \tag{37}$$

By an analysis similar to the one we have just gone through it can be verified that the other time orderings do not have factorable exponentials in which $E_0^N - E_n^N$ appear.

In general, G_2 can be written

$$G_2(1, 2; 1', 2') = G_2(1, 2; 1', 2')^{\mathrm{I}}\Theta(\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) + G_2(1, 2; 1', 2')^{\mathrm{II}}\Theta(-\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) + \text{other orderings} \tag{38a}$$

where the Heaviside functions satisfy the time orderings of Case I and II above. Let us define the first two terms as the *hole–particle Green's function*,

$$\begin{aligned} G^{\mathrm{hp}}(1, 2; 1', 2') = &-\sum_n \exp\,[i(E_0^N - E_n^N)\tau]\chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)\tilde{\chi}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \\ &\times \Theta(\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) \\ &-\sum_n \exp\,[-i(E_0^N - E_n^N)\tau]\tilde{\chi}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)\chi_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \\ &\times \Theta(-\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|). \end{aligned} \tag{38b}$$

The spectral representation of G_2 is obtained from (38b) by using (29b) and Fourier transforming the variable τ, as in Eq. (14), to give

$$G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega) = G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega)^{\mathrm{I}} + G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega)^{\mathrm{II}} + \text{other terms} \tag{39}$$

where

$$\begin{aligned} &G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega)^{\mathrm{I}} \\ &= \frac{1}{i}\lim_{\eta \to +0} \sum_n \frac{\chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)\tilde{\chi}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2)}{\omega - (E_n^N - E_0^N) + i\eta} \\ &\quad \exp\left\{+\frac{i}{2}[\omega - (E_n^N - E_0^N)](|\tau_1| + |\tau_2|)\right\} \end{aligned} \tag{40a}$$

and

$$\begin{aligned} &G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega)^{\mathrm{II}} \\ &= -\frac{1}{i}\lim_{\eta \to +0} \sum_n \frac{\chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)\chi_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2)}{\omega + (E_n^N - E_0^N) - i\eta} \\ &\quad \times \exp\{-(i/2)[\omega + (E_n^N - E_0^N)][|\tau_1| + |\tau_2|]\}. \end{aligned} \tag{40b}$$

Consequently

$$G_2^{\mathrm{hp}}(\omega) = G_2(\omega)^{\mathrm{I}} + G_2^{\mathrm{II}}(\omega).$$

Let us define a new variable ω_n which runs through all $E_n^N - E_0^N$ and all $E_0^N - E_n^N$ values. Correspondingly sgn $(\omega_n) = 1$ and sgn $(\omega_n) = -1$.

Let us define

$$\begin{aligned} X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) &= \chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) \qquad \text{for} \quad \omega_n > 0 \\ X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) &= \tilde{\chi}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) \qquad \text{for} \quad \omega_n < 0 \end{aligned} \tag{40c}$$

and

$$\begin{aligned} \tilde{X}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) &= \tilde{\chi}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) \qquad \text{for} \quad \omega_n > 0 \\ \tilde{X}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) &= \chi_n(\mathbf{r}_1, \mathbf{r}_1'; \tau) \qquad \text{for} \quad \omega_n < 0 \end{aligned}$$

Let us define

$$X_n(1, 1') = e^{-i\omega_n t'} X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)$$

where $t' = \frac{1}{2}(t_1 + t_1')$ and

$$\tilde{X}_n(1, 1') = e^{i\omega_n t'} \tilde{X}_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1)$$

then

$$\begin{aligned} &G_2^{\mathrm{hp}}(1, 2; 1', 2') \\ &= -\sum_{\omega_n > 0} X_n(1, 1')\tilde{X}_n(2, 2')\Theta(\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) \\ &\quad -\sum_{\omega_n < 0} X_n(1, 1')\tilde{X}_n(2, 2')\Theta(-\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) \\ &= -\sum_{\omega_n} X_n(1, 1')\tilde{X}_n(2, 2')\Theta(\mathrm{sgn}\,(\omega_n)\tau - \tfrac{1}{2}|\tau_1| - \tfrac{1}{2}|\tau_2|) \end{aligned}$$

and

$$G_2^{hp}(\tau_1, \tau_2, \omega) = \frac{1}{i} \lim_{\eta \to +0} \left\{ \sum_{\omega_n > 0} \frac{X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1) \tilde{X}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \operatorname{sgn}(\omega_n)}{\omega - \omega_n + i\eta \operatorname{sgn}(\omega_n)} \right.$$
$$\left. + \sum_{\omega_n < 0} \frac{X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1) \tilde{X}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \operatorname{sgn}(\omega_n)}{\omega - \omega_n + i\eta \operatorname{sgn}(\omega_n)} \right\}$$
$$\times \exp\left\{ \frac{i}{2} \operatorname{sgn}(\omega_n)[\omega - \omega_n][|\tau_1| - |\tau_2|] \right\}$$
$$= \frac{1}{i} \lim_{\eta \to +0} \sum_{\omega_n} \frac{X_n(\mathbf{r}_1, \mathbf{r}_1'; \tau_1) \tilde{X}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2) \operatorname{sgn}(\omega_n)}{\omega - \omega_n + i\eta \operatorname{sgn}(\omega_n)}$$
$$\times \exp\left\{ \frac{i}{2} \operatorname{sgn}(\omega_n)[\omega - \omega_n][|\tau_1| + |\tau_2|] \right\} \tag{40d}$$

and obviously (38) becomes

$$G_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega) = G_2^{hp}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; \tau_1, \tau_2, \omega) + \text{other terms.} \tag{40e}$$

The "other terms" of G_2 have poles at real ω values that differ from $\pm(E_n^N - E_0^N)$. Therefore, while (39) does not have Heaviside functions to distinguish its terms, they all have poles at different positions in the complex ω plane.

In this work we shall concentrate on G_2^{hp} of Eq. (38b) and use it in the next section to obtain an equation for X_n.

The information contained in G_2^{hp} is clear, namely its poles give the target *excitation (or deexcitation) energies*. As interesting is that the residue of G_2^{hp} at the nth pole gives $X_n(\mathbf{r}, \mathbf{r}'; \tau)$ which is, from (35), in the limit $\tau \to -0$, just the matrix element $\langle \Psi_0^N | \psi^\dagger(\mathbf{r}')\psi(\mathbf{r}) | \Psi_n^N \rangle$. This is a case which shall be, in practice, obtained in our approximate solutions (see Section IV). This residue then allows the calculation of all *one-particle transition matrix elements* between Ψ_0^N and Ψ_n^N. If

$$Op^{(1)} = \sum_i Op^{(1)}(\mathbf{r}_i)$$

then in second quantized form

$$Op^{(1)} = \int d\mathbf{r} \psi^\dagger(\mathbf{r}) Op^{(1)}(\mathbf{r}) \psi(\mathbf{r})$$
$$= \int d\mathbf{r}\, d\mathbf{r}' \psi^\dagger(\mathbf{r}') Op^{(1)}(\mathbf{r}) \psi(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}').$$

Therefore

$$\langle \Psi_0^N | Op^{(1)} | \Psi_0^N \rangle = \int d\mathbf{r}\, d\mathbf{r}' Op^{(1)}(\mathbf{r}) \langle \Psi_0^N | \psi^\dagger(\mathbf{r}')\psi(\mathbf{r}) | \Psi_n^N \rangle \delta(\mathbf{r} - \mathbf{r}')$$

where the integral over the δ function is taken only after the operator is applied. In particular, from (10), $\langle \Psi_0 | \psi^\dagger(\mathbf{r})\psi(\mathbf{r}) | \Psi_n \rangle$ the diagonal element in the position representation is just $\langle \Psi_0 | \rho(\mathbf{r}) | \Psi_n \rangle$ the transition density. Moreover, if our Fourier transforms Eq. (9) to get

$$\rho_{\mathbf{k}} = \sum_{i=1}^N \int d\mathbf{r}\, \delta(\mathbf{r} - \mathbf{r}_i) e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i}$$

it is seen that the Fourier transform with respect to $\mathbf{r}$ of the element

$$\langle \Psi_0^N | \psi^\dagger(\mathbf{r})\psi(\mathbf{r}) | \Psi_n^N \rangle$$

is just

$$\langle \Psi_0^N | \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i} | \Psi_n^N \rangle$$

the generalized oscillator strength (Schneider, 1970).

Therefore the pole and residues of the hole-particle part of the two-particle Green's function, in the form in which they shall be obtained by the approximation methods to be given later, shall yield the excitation energies, the generalized oscillator strengths, and enable one to calculate all one-particle transition matrix elements.

To calculate expectation values of n-particle operators ($n > 1$) other than H, in the ground or in excited states takes a knowledge of higher Green's functions and the rest of G_2. These are more difficult to calculate in the sense that the nonperturbative approximation to be discussed in Section IV will not yield this information. As such this review will not discuss these quantities though, in principle, extensions of the perturbative methods of Section V could formally, but at this time probably not practically, calculate them.

It is now time to turn to the question of calculating G_1 and G_2, in principle, exactly. Certainly their calculation is now amply justified.

III. Coupled System of Equations for Green's Functions (The Method of Functional Differentiation; The Dyson Equation; The Bethe–Salpeter Equation)[11]

A. A System of Equations for the Many-Particle Green's Function

In this section various useful and equivalent forms of the *equations of motion for G_1 and G_2 shall be given.*

To determine the equation of motion for G_1, the time-derivative of G_1 is

[11] Galitski and Migdal (1958). For further references see Pines (1961), Abrikosov *et al.* (1963), Matsubara (1955), Martin and Schwinger (1959); for an introduction see Kadanoff and Baym (1962), Migdal (1967), Falkoff (1962), Roman (1965), Kirzhnits (1967), March *et al.*(1967), Mattuck (1967).

needed. In the definition of G_1 the time only appears in the ψ and $\psi^\dagger$ (and in the time ordering) so it is evident that $\partial\psi^\dagger/\partial t$ is needed. Since ψ is a Heisenberg operator, its equation of motion is

$$i(\partial/\partial t)\psi(\mathbf{r}t) = [\psi(\mathbf{r}t), H]. \tag{41}$$

To evaluate the commutator in (41) one substitutes the second quantized form of H in the Heisenberg representation into the commutator bracket. The resulting commutator, now only between $\psi(\mathbf{r}t)$ and the annihilation and creation operators coming from H can be evaluated, after a little algebra, by using the anticommutation relations between Fermi–Dirac particles, Eq. (4) and integrating over the resulting δ functions, yielding

$$i(\partial/\partial t)\psi(\mathbf{r}t) = \left\{h(\mathbf{r}) + \int d\mathbf{r}'\psi^\dagger(\mathbf{r}'t)V(|\mathbf{r}-\mathbf{r}'|)\psi(\mathbf{r}'t)\right\}\psi(\mathbf{r}t) \tag{42}$$

where h will symbolize the one-electron parts of H. One should note that Eq. (42) is of the form of a *time dependent one-particle Schroedinger equation for* $\psi(\mathbf{r}t)$ (the Schroedinger matter field). A useful shorthand notation is obtained using the definitions

$$1 \equiv \mathbf{r}_1, t_1 \qquad 2 \equiv \mathbf{r}_2, t_2 \qquad V(1-2) \equiv V(|\mathbf{r}_1 - \mathbf{r}_2|)\delta(t_1 - t_2)$$

and

$$d1 = d\mathbf{r}_1\, dt_1$$

With this, (42) becomes

$$[i(\partial/\partial t_1) - h(1)]\psi(1) = \int d2V(1-2)\psi^\dagger(2)\psi(2)\psi(1). \tag{42'}$$[12]

Now differentiating Eq. (6) with respect to t_1' (note $\partial\Theta(t)/\partial t = \delta(t)$), gives

$$i\frac{\partial G_1(1,1')}{\partial t_1} = \langle\Psi_0|\delta(t_1 - t_1')[\psi(1), \psi^\dagger(1')]_+|\Psi_0\rangle + \langle\Psi_0|T\left(\frac{\partial\psi(1)}{\partial t_1}, \psi^\dagger(1')\right)|\Psi_0\rangle. \tag{43}$$

Introducing the definition

$$\delta(1-1') = \delta(\mathbf{r}_1 - \mathbf{r}_1')\delta(t_1 - t_1') \tag{44}$$

using (4) and (42') (for G_1) gives

$$i(\partial/\partial t_1)G_1(1,1') = \delta(1-1') + h(1)G_1(1,1') - \int d2V(1-2)\langle T(\psi^\dagger(2)\psi(2)\psi(1)\psi^\dagger(1'))\rangle. \tag{45}$$

[12] Different forms of the same equation shall be given the same number with primes to distinguish them.

The matrix element in the last term on the right-hand side can be related to G_2, if a positive infinitesimal time "ε" is added to t_2 in $\psi^\dagger(2)$ and the limit $\varepsilon \to 0$ is inserted inside the integral sign. Now that there are two different indices $\mathbf{r}_2, t_2 + \varepsilon(\mathbf{r}_2, t_2 + \varepsilon \equiv 2^+)$ and 2, permutations of time ordering under T can be made as discussed in the previous section. These permutations are made to give the ordering as in G_2, with the result that (45) becomes

$$\left[i\frac{\partial}{\partial t} - h(1)\right]G_1(1,1') + i\int d2V(1-2)G_2(1,2;1',2^+) = \delta(1-1'), \tag{46}$$

where "2^+" implies that the limit $2^+ \to 2$ ($\varepsilon \to 0$) must be taken before integration. *This equation is the first equation in the coupled hierarchy relating* G_n *to* G_{n+1} *and* G_{n-1}. The rest of the hierarchy can be derived by analogous methods, i.e., differentiating the definition of G_n with respect to t_1, commuting, rearranging, etc., to express the ground state matrix elements on the right-hand side in terms of G_{n+1} and the lower order G_k's. This coupled hierarchy is the new form of the Schroedinger equation in Green's function theory.

B. The Dyson Equation and the Self-Energy

Now, in preparation for the derivations and approximations in the next section it is useful to write some *other exact forms of the equation for* G_1. To do this it is efficient to define an unperturbed (i.e., V is temporarily set equal to zero in the Hamiltonian) one particle Green's function G_1^0 by

$$[G_1^0(1,1')]^{-1} \equiv \left[i\frac{\partial}{\partial t_1} - h(1)\right]\delta(1-1'). \tag{47a}$$

Inserting (47a) into (46) gives

$$\int d1''[G_1^0(1,1'')]^{-1}G_1(1'',1') + i\int d2V(1-2)G_2(1,2;1',2^+) = \delta(1-1'). \tag{46'}$$

The integral kernels in (46') can be thought of as matrices with continuous indices 1, 1', etc., thus implying an operator equation

$$[G_1^0]^{-1}G_1 + iVG_2 = I. \tag{46''}$$

When (46'') is multiplied by G_1^0 from the left

$$G_1 = G_1^0 + iG_1^0VG_2 \tag{46'''}$$

which is an *integral equation form of the equation of motion*, i.e.,

$$G_1(1,1') = G_1^0(1,1') + i\int d2\,d2'G_1^0(1,2)V(2-2')G_2(2,2';1',2^+). \tag{46^{IV}}$$

Operating from the right on (46'') with G_1^{-1} gives

$$[G_1^0]^{-1} + iVG_2G_1^{-1} = G_1^{-1} \tag{46^{V}}$$

a form which lends itself to the introduction of a new function: Σ *called the self energy, the optical potential,* or the one-particle effective potential defined as

$$\Sigma = -iVG_2G_1^{-1} \tag{47b}$$

or

$$\Sigma(1, 1') = -i\int d2\, d2' V(1-2)G_2(1, 2; 2', 2^+)G_1^{-1}(2', 1'). \tag{47b'}$$

With (47b), Eq. (46^{v}) can be written as

$$G_1^{-1} = [G_1^0]^{-1} + \Sigma. \tag{48}$$

Multiplying on the right by G_1 gives

$$[G_1^0]^{-1}G_1 - \Sigma G_1 = I \tag{48'}$$

or

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right]G_1(1, 1') - \int d2\Sigma(1, 2)G_1(2, 1') = \delta(1-1'). \tag{48''}$$

Multiplying Equation (47b) from the right by G_1 and inserting the results in (46$'''$) gives

$$G_1 = G_1^0 + G_1^0\Sigma G_1. \tag{48'''}$$

Equations (48$''$), (48$'''$), and (48) are, respectively, the differential, integral, and operator forms of the equation of motion for G_1 and are called the *Dyson equation.* In the Dyson equation G_2 is replaced, using (47b), by Σ and so the determination of G_1 and G_2 becoming equivalent to the determination of Σ and G_1. Hence a change of functional variables has been made. It will soon be seen that the reason for changing unknown functions is that our intuition as to approximate forms for G_2 is not as well developed as it is for Σ. One sees from (48) that the Dyson equation, or the one-particle equation is closed for G_1 if Σ is known and that Σ plays the role of an effective potential, which is generally energy dependent, complex and nonlocal. Clearly, G_1 is not a true Green's function[13] in that only if Σ is a local, energy-independent potential does one obtain the usual "operator times a Green's function equal to a delta function" relation, but is rather a "driven" Green's function equation. It should be realized that (48) is a one-particle equation, which if Σ is known is equivalent to the Schroedinger equation. The effective one-particle potential has folded in it all the effects of the rest of the system; as such, it would indeed be surprising if it were not complex, nonlocal, and

[13] By "true" Green's function we mean the usual Green's function discussed in mathematical physics in connection with differential equations.

energy-dependent. Thus, an exact one-particle picture has been achieved at the price of a complicated potential. A detailed study of Σ will show it to be real when ω is set to an energy value below the first inelastic threshold of the system. Above the threshold Σ is complex, the complex part can be shown (Mott and Massey, 1965) to represent the absorption of incident particles by the system. Since we are working with an effectively closed equation for G_1, which in turn starts and ends in $|\Psi_0\rangle$, inelasticity must be taken into account by an absorption potential. Since such phenomenological potentials play a key role in optics, they are called optical potentials.

At this point, it shall be assumed that Σ is known and the method of solving (48) shall be discussed, after which the discussion will return to the question of finding Σ.

It will be useful to *Fourier transform the time variable* in (48$''$). It should be noted that $\Sigma(1, 1')$ depends on $t_1 - t_1'$ only, since from (48) it has the same time variable as G_1 and G_1^0 which have this property. Using (14) and the Fourier convolution theorem, (48$''$) becomes

$$[\varepsilon - h(\mathbf{r})]G(\mathbf{r}, \mathbf{r}'; \varepsilon) - \int d\mathbf{r}_2\Sigma(\mathbf{r}, \mathbf{r}_2; \varepsilon)G(\mathbf{r}_2, \mathbf{r}'; \varepsilon) = \delta(\mathbf{r} - \mathbf{r}') \tag{49}$$

As is well known, Green's functions are more difficult to solve for than wave functions since they are basically nondiagonal matrix equations. As such it is reasonable to seek what is always sought in such cases, an eigenfunction expansion which diagonalizes Eq. (49). To do this, it is pedagogically useful to define an integral operator (Layzer, 1963)

$$L = h + \Sigma$$

and to write Eq. (49) symbolically as

$$[\varepsilon - L(\varepsilon)]G(\varepsilon) = I. \tag{49'}$$

Since L is generally non-Hermitian, G admits a biorthogonal expansion (Morse and Feshbach, 1953) in the assumed complete set of eigenfunctions $\varphi_n(\varepsilon)$ and $\bar{\varphi}_n(\varepsilon)$ of $L(\varepsilon)$ and its adjoint $L^\dagger(\varepsilon)$, respectively, of the form, for a given ε

$$G(\varepsilon) = \sum_n \frac{\varphi_n(\varepsilon)\bar{\varphi}_n(\varepsilon)}{\varepsilon - E_n(\varepsilon)}. \tag{50}$$

If (50) is put into (49) and its adjoint, respectively, and the limit $\varepsilon \to E_n(\varepsilon)$ taken, the set of equations obtained are

$$\begin{aligned}[L(\varepsilon) - E_n(\varepsilon)]\varphi_n(\varepsilon) &= 0\\ [L^\dagger(\varepsilon) - E_n^*(\varepsilon)]\bar{\varphi}_n(\varepsilon) &= 0\end{aligned} \tag{51}$$

with the biorthogonality condition appearing as

$$\langle \varphi_n(\varepsilon) | \bar{\varphi}_m(\varepsilon) \rangle = \delta_{mn}. \tag{52}$$

The detailed forms of Eqs. (51) are

$$h(\mathbf{r})\varphi_n(\mathbf{r}\varepsilon) + \int d\mathbf{r}'\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon)\varphi_n(\mathbf{r}'\varepsilon) = E_n(\varepsilon)\varphi_n(\mathbf{r}\varepsilon)$$

$$h(\mathbf{r})\bar{\varphi}_n(\mathbf{r}\varepsilon) + \int d\mathbf{r}'\bar{\varphi}_n(\mathbf{r}'; \varepsilon)\Sigma^*(\mathbf{r}', \mathbf{r}; \varepsilon) = E_n^*(\varepsilon)\bar{\varphi}_n(\mathbf{r}\varepsilon). \tag{51'}$$

For the nonperturbative methods of this review, (51′) shall be the form of the Dyson equation that will be used to determine the one-particle Green's function via the $E_n(\varepsilon)$, $\varphi_n(\varepsilon)$, and $\bar{\varphi}_n(\varepsilon)$. Equations (48) will be of formal use. While (51′) is a strange beast in theoretical chemistry and atomic and molecular physics, it is important to emphasize that the eigenvalue problem for non-Hermitian matrices can be solved by techniques which are standard in the applied mathematics literature (Wilkinson, 1965). In principle this non-Hermitian eigenvalue problem must be solved for each and every value of ε in the complex plane. Each ε gives a complete set of eigenfunctions and eigenvalues. Clearly, if all this were needed to represent Eq. (50) the method would be impractical. The saving grace is that as seen in Eq. (31) $G(\varepsilon)$ can be represented in a form where all the energy dependence comes into the denominator. In (31) only one set of functions $\{f, g\}$ as well as a specific set of energies are needed for all real ε. Of course for complex ε the poles of G in (32) must be found so as to allow analytic continuation to achieve a complete complex plane representation. Hence, to obtain a form in the spirit of (31) it is desirable to use (51) to solve for the poles and residues of (50) and then to use the Mittag–Leffler theorem to represent $G(\varepsilon)$ in terms of its residues and poles [$G(\omega)$ is analytic on the double-sheet except for poles]. Now a great deal is actually known about the poles of $G(\varepsilon)$. From the discussion of Eq. (31) it was seen that:

(a) For an *infinite system*, branches exist parallel to, but $i\eta$ above and below the real axis, in the second and fourth quadrants of the physical sheet. Therefore, all poles must lie on the nonphysical sheets, and the residues of these singularities are not simply related to the $\{f, g\}$ set which are related to the branch cut.

(b) For *finite atomic and molecular systems*, the branch cuts are replaced by a set of poles and adjoining branch cuts. Poles can exist on the physical sheet, as well as on the nonphysical sheets reached by continuing across the cut. The physical poles are clearly related to residues which are $g_n g_n^*$ from Eq. (31).

(c) For a *finite system described approximately by a finite basis set*, both the branches are replaced by poles, since the effect of the finite basis set is

to put the system into the Hilbert-space "box" spanned by the set and hence to give only a discrete spectrum. In this latter case the poles are real (in the limit $\eta \to 0$) and from Eq. (31) correspond to ionization and electron-affinity energies. The residues are clearly related to $g_n g_n^*$ and $f_n f_n^*$.

Now in atomic and molecular physics experience has shown that ground state problems, response functions, and even effective scattering potential problems, can be represented by discrete basis sets which span (in a mean value sense) the short range region of real space (physical or configurational) in which the particles of the system are simultaneously interacting. It is in this region that the dynamics of the problem occur. The continuum relates the system to boundary conditions which describe the experiment being done on the system. Therefore, to solve for Σ and G_1, which characterize the system, it will be physically reasonable and practical to use finite basis sets; in particular, those bases known to give good energies, correlations, response functions (i.e., polarizabilities), etc. In the case (c) that concerns this review, a comparison of (31) and (8) shows that the poles occur near the real axis at solutions of

$$\varepsilon_n = E_n(\varepsilon_n). \tag{52}$$

The residues of the Green's function at the poles are obtained by the standard procedure under the assumption that Eq. (50) has only simple poles. That is, it is assumed that there are no contributions from singularities in the energy dependence of $\varphi_n(\varepsilon)$, $\bar{\varphi}_n(\varepsilon)$, and $E_n(\varepsilon)$. Thus applying the standard formula for the residue of a simple pole

$$\lim_{\varepsilon \to \varepsilon_n} (\varepsilon - \varepsilon_n)G(\varepsilon)$$

to the Green's function in (50) the residue at the nth pole $\varepsilon_n = E_n(\varepsilon_n)$ is

$$\Gamma_n \varphi_n(\varepsilon_n)\bar{\varphi}_n(\varepsilon_n) \tag{53a}$$

where

$$\Gamma_n^{-1} = [1 - (d/d\varepsilon)E_n(\varepsilon)]_{\varepsilon=\varepsilon_n},$$

that is, Γ_n is the residue of $1/[\varepsilon - E_n(\varepsilon)]$ taken at the ε_n pole. Hence

$$G(\varepsilon) = \sum_n \frac{\Gamma_n \varphi_n(\varepsilon_n)\bar{\varphi}_n(\varepsilon_n)}{\varepsilon - \varepsilon_n}. \tag{53b}$$

Clearly in case (c) the φ_n are related to the g's and f's. The ε_n with $\mathrm{Re}\,\varepsilon_n < 0$ give residues $g_n g_n^*$ and with $\mathrm{Re}\,\varepsilon_n > 0$ give residues $\Gamma_n \varphi_n \bar{\varphi}_n$. Thus to get $G(\varepsilon)$ for case (c) it is, in principle, necessary to solve Eq. (51′) for all real ε and to choose from the complete spectrum those φ's and E's satisfying the eigenvalue

equation (52) (we shall discuss the finding of Γ_n shortly). In practice one will solve at a finite set of real ε values and extrapolate between them or for a finite basis set the determinant associated with (52) will be solved for. Since, as will be seen, Eq. (51′) and the equation to be derived for Σ will be solved iteratively and self-consistently, the first approximation for G will be taken as that of the Hartree–Fock model. In this model the ε_n are the Hartree–Fock bond and virtual orbital energies. It should be noted that for the Hartree–Fock model (or indeed for any true single particle model) all $\Gamma_n = 1$, since the model is a solution to an energy-independent effective potential. These Hartree–Fock poles can be used as a grid of ε points on the next iterate. As in any iterative method a reasonable first guess, which the Hartree–Fock model is, is needed for convergence, thus it is hoped that the final poles will not differ greatly (in the mean) from the initial guess. This will simplify the search for ε_n. To find Γ_n it is necessary to know $E_n(\varepsilon)$ in the neighborhood of the poles, but this is just what the extrapolation procedure will give us. Then knowing this one can find $\partial E_n/\partial\varepsilon$ numerically.

It is perhaps worth stressing that a method to solve for $G_1(\varepsilon)$ for a given Σ has now been sketched out. In doing this for the physical reasons discussed above it has been assumed that a finite discrete basis set will be adequate to represent Σ and G_1. Mathematically this means that the branch cut has been replaced by a discrete set of poles on the real axis. This can be done if it is assumed that (a) the poles far from the real axis do not affect the physics and (b) that the $\varphi_n(\varepsilon)$ and $\bar{\varphi}_n(\varepsilon)$ do not give poles themselves. The former is justified (Goldberger and Watson, 1964) because poles far from the real axis describe effects that take place in extremely short times relative to the times for the total process, e.g., for a scattering process they describe events that occur before the particle fired from the gun can arrive at the target. The latter assumption follows from the idea that the $\varphi_n(\varepsilon)$'s are effective, one-particle orbitals for a given energy. If a singularity existed a small change in ε would cause large changes in $\varphi_n(\varepsilon)$ which would die out as ε is changed again, infinitesimally. This is similar to an extremely narrow resonance phenomenon which would not be observable in the finite resolution measuring processes used in experiments. In other words, if such poles existed they would not effect observables.

Assumption (a) is further justified by realizing that a pole near the cut causes a heavy weighting of the continuum functions in the neighborhood of the pole. This weighting is analogous to forming a wave packet out of the functions near the pole. The discrete basis essentially says that if only such poles exist, the spectral density result and packeting phenomenon can be anticipated by trying to represent the packets themsleves with a finite discrete function (calculated from a finite range basis). For poles far from the cut the wave packet is very broad containing contributions from a wide range of

continuum functions. Such broad resonance type phenomena result in little change in the spectral density and are essentially unobservable. Once the poles and residues of G_1 are known the integrals for $\rho(\mathbf{r}, \mathbf{r}')$ and E_0 are easily done.

C. Hierarchies for Green's Functions and Related Quantities; the Method of Functional Differentiation

Now that G_1 is known given Σ, equations for finding G_2 or Σ must be developed. In the spirit that the equations for $G_1, G_2, \ldots$, or $G_1, \Sigma, \ldots$, will be solved simultaneously, it will be assumed that G_1 is known and an equation for G_2 or Σ shall be the object of this subsection. Clearly the equation for G_2 or Σ will involve a knowledge of G_3 or its equivalent. As in the case of G_1, physical insight and incisive approximation will be facilitated by writing the equation for G_2 in terms of a closed equation with an effective (two-particle in the media) potential (the knowledge of which is equivalent to having G_3) called Ξ. Several sets of equivalent functional variables are in the process of being defined, viz., $G_1, G_2, G_3, \ldots$; $G_1, G_2, \Xi, \ldots$; $G_1, \Sigma, \Xi, \ldots$; $G_1, \Sigma, G_3, \ldots$; $G_1, \Sigma, \delta\Sigma/\delta U, \ldots$; $\{\varphi_n, \varepsilon_n\}, \Sigma, \Xi, \ldots$; etc. The *various hierarchies* are all, of course, formally equivalent, in the sense that no new physical content will be contained in any of the alternative forms to the $G_1, G_2, G_3, \ldots$ set of coupled equations. However, since the set of coupled equations must be truncated by an approximation at some stage, different forms of the hierarchy lead naturally to different approximations, and hence to different truncation procedures.

In Section VI, perturbation expressions are derived which give G_2 or Σ in terms of V and G_1. It will be pointed out in Section VI that the perturbation expansion for G_2 (or Σ) in terms of G_1, and the Dyson equation for G_1 form self-consistent perturbation theories for G_1 and G_2. The perturbation expansion for G_3 involves G_2 and G_1. The two closed equations for G_1 and G_2 and the expansion for G_3 again give a self-consistent perturbation theory of higher order. Of course, closing the set of equations at G_3 will be much more work than closing at G_2. Only experience will show how high in the coupled equations the truncations must be made. Fortunately, since anything above G_2 will be inordinately difficult to calculate, diagrammatic analysis and experience (Kelly, 1968; Karplus and Caves, 1969) tends to indicate that G_3 will not be needed for most atomic and molecular problems. The completion of the G_3 truncation perturbative strategy does not require the derivation of the closed equation for G_2 in terms of Ξ since it has already been indicated how the equation for G_2 in terms of G_3 is derived. The closed equation from the perturbative point of view is only an alternate equation in the sense that (48) is an alternate to (46). The real reason that this closed alternate form will be derived is to introduce the *method of functional differentiation*

and the expression of G_2 in terms of functional derivatives of lower order quantities. This method will lead to nonperturbative approximations to be discussed in the fifth section.[14] The fundamental idea of the functional derivative method of Schwinger is (Schwinger, 1951; Galitski and Migdal, 1958) to introduce into the problem an arbitrary nonlocal time dependent potential $U(1, 1')$, that is turned on slowly (adiabatically) at $t = -\infty$ and off at $t = +\infty$. This potential "probes" the system, and the physical quantities G_1, G_2, Σ, etc., are calculated in the limit $U(1, 1') \to 0$. The idea is exactly that of studying generalized response properties of the system. The method is quite physical in that all experiments actually probe the system and measure its response in one of its several forms, e.g., absorption coefficient, dielectric constant, etc. It shall be shown that G_2 (for a given G_1) can be replaced by a knowledge of $\delta G_1/\delta U|_{U\to 0}$ i.e., the variation of G_1 with respect to the small probe potential in the limit that the potential goes to zero. What will result is a sequence of coupled equations relating Σ (or G_2) to $\delta\Sigma/\delta U$; $\delta\Sigma/\delta U$ to second derivatives, etc. It is worth repeating that the advantages of the new hierarchy over the original one are both physical and formal.

Physical arguments will allow one to make approximations to variations that were not evident when G_3, G_4, etc., were used. The idea, as will be seen, is that approximations to Σ and G_2 that are inadequate to represent Σ and G_2 themselves may suffice to calculate small variations in Σ and G_2. The formal advantage of the method is that closed equations for G_2, etc., can be derived without invoking perturbational diagrammatic summation procedures.

In the situation that a small arbitrary external nonlocal two time-dependent potential $U(2', 2)$ of the form

$$U(2', 2) = U(\mathbf{r}_2'\mathbf{r}_2', \mathbf{r}_2 t_2)\Theta(t_2' - t_2)$$

(where the Heaviside function maintains t_2 earlier than t_2') is turned on at $t = -\infty$ and off at $t = +\infty$

$$G_1(1, 1'; U) = \frac{1}{i}\langle\Psi_0(U)|T(\psi_U(1)\psi_U^\dagger(1')|\Psi_0(U)\rangle \tag{54}$$

where the symbol U reminds us that the new Hamiltonian has $U(2', 2)$ added to the one of the previous section. Since the defining equation was for an arbitrary Hamiltonian, the derivation still holds and the equation can be written as

$$G^{-1}(U) = [G_1^0]^{-1} - U - \Sigma. \tag{55}$$

[14] Historically the equation for G_2 in terms of Ξ, was first derived by Bethe and Salpeter, using formal complete diagrammatic perturbation summations. The method chosen here has the advantage of giving functional derivative expression for Ξ and leads to approximations that might not be obvious in the diagrammatic formalism.

We can consider U as a functional variable and we can form the functional derivative of a functional of U. The exact definition of the functional derivative will be given in Appendix A as well as the derivation of the fundamental equation (Schwinger, 1951) for the functional derivative of $G_1(U)$. We note that if F is a functional of $U(x)$ of the form

$$F[U(x)] = \int dx K(x)U(x)$$

then the functional derivative of F with respect to U is

$$\delta F/\delta U(x) = K(x).$$

In Appendix A we derive the *Schwinger equation* which will be of fundamental importance in the following

$$\left.\frac{\delta G_1(1, 1'; U)}{\delta U(2', 2)}\right|_{U=0} = -G_2(1, 2; 1', 2') + G_1(1, 1')G_1(2, 2') \tag{56a}$$

and as a special case for a local potential

$$\left.\frac{\delta G_1(1, 1'; U)}{\delta U(2)}\right|_{U=0} = -G_2(1, 2; 1', 2^+) + G_1(1, 1')G_1(2, 2^+). \tag{56b}$$

This is the desired functional relation that for a given G_1 replaces G_2 by $\delta G_1/\delta U|_{U=0}$.

For a given G_1, the derivation of the hierarchy for Σ in terms of $\delta\Sigma/\delta U$ is easily carried through. Since

$$\int d2 G(1, 2)G^{-1}(2, 1') = \delta(1 - 1')$$

taking the variational derivative with respect to $U(4, 5)$ yields

$$\int d2\left\{\frac{\delta G(1, 2)}{\delta U(4, 5)}G^{-1}(2, 1') + G(1, 2)\frac{\delta G^{-1}(2, 1')}{\delta U(4, 5)}\right\} = 0$$

which can be multiplied from left by $G(1', 2')$ and integrated over $d1'$ to give

$$\frac{\delta G(1, 2')}{\delta U(4, 5)} = -\int d2\, d1' G(1, 2)\frac{\delta G^{-1}(2, 1')}{\delta U(4, 5)}G(1', 2'). \tag{57}$$

To evaluate $\delta G^{-1}/\delta U$ Eq. (55) is varied giving

$$\frac{\delta G^{-1}(2, 1')}{\delta U(4, 5)} = -\delta(2 - 4)\,\delta(1' - 5) - \frac{\delta\Sigma(2, 1')}{\delta U(4, 5)} \tag{58}$$

Substituting (58) into (57) gives

$$\frac{\delta G(1, 2')}{\delta U(4, 5)} = G(1, 4)G(5, 2') + \int d2\, d1' G(1, 2)\frac{\delta\Sigma(2, 1')}{\delta U(4, 5)}G(1', 2') \tag{59}$$

which on using (56a) gives

$$-G_2(1,5;2',4)+G_1(1,2')G_1(5,4)=G_1(1,4)G_1(5,2')+\int d2\,d1'G_1(1,2)\frac{\delta\Sigma(21')}{\delta U(4,5)}G_1(1',2'). \tag{60a}$$

Equation (60a) is the promised equation which replaces G_2 by $\delta\Sigma/\delta U$. Again the special case of a local potential is

$$-G_2(1,4;2',4^+)+G_1(1,2')G_1(4,4^+)=G_1(1,4)G_1(4,2)+\int d2\,d1'G_1(1,2)\frac{\delta\Sigma(2,1')}{\delta U(4)}G_1(1',2'). \tag{60b}$$

We can now substitute $\delta\Sigma/\delta U$ for G_2 in the definition of Σ, Eq. (47b). It should be noted that in this definition $G_2(1,2;1',2^+)$ the so-called "three-point" Green's function appears rather than the more general "four-point" Green's function $G_2(1,2;1',2')$ because the two-particle potential in the Hamiltonian is a two-point instantaneous potential (in the case of more general four-point retarded or advanced potentials the more general four-point Green's function appears). Thus, in the hierarchy for Σ in terms of $\delta\Sigma/\delta U$ only local potentials as in Eq. (60b) need be used. However, to develop a closed equation for the general four-point G_2 in terms of Ξ the more general functional derivative in terms of a nonlocal two-time potential will be needed. Hence, substituting (60b) into (47b)

$$\begin{aligned}\Sigma(1,1')&=-i\int d1''\,d2V(1-2)G_2(1,2;1'',2^+)G_1^{-1}(1'',1')\\&=i\int d1''\,d2V(1-2)\Big\{G_1(1,2)G_1(2,1'')-G_1(1,1'')G_1(2,2^+)\\&\quad+i\int d3\,d4G_1(1,3)\frac{\delta\Sigma(3,4)}{\delta U(2)}G_1(4,1'')\Big\}G_1^{-1}(1'',1')\\&=i\int d2V(1-2)\Big\{G_1(1,2)\,\delta(2-1')-G_1(2,2^+)\,\delta(1-1')\\&\quad+i\int d3\,d4G(1,3)\frac{\delta\Sigma(3,4)}{\delta U(2)}\delta(4-1')\Big\}\\&=-i\,\delta(1-1')\int d2V(1-2)G_1(2,2^+)\\&\quad+iV(1-1')G_1(1,1'^+)\\&\quad+i\int d2\,d3V(1-2)G_1(1,3)\frac{\delta\Sigma(3,1')}{\delta U(2)}.\end{aligned} \tag{61}$$

Equation (61) is the first equation of a new hierarchy which for a given G_1, replaces the coupled equations for G_2 in terms of G_3, G_3 in terms of G_4, etc., with equations relating Σ to $\delta\Sigma/\delta U$, $\delta\Sigma/\delta U$ to second variations, etc. Higher equations in the hierarchy are obtained by functionally differentiating (61). For example, the first variation yields

$$\begin{aligned}\frac{\delta\Sigma(1,1')}{\delta U(2)}&=-i\,\delta(1-1')\int d3V(1-3)\frac{\delta G(3,3^+)}{\delta U(2)}\\&\quad+iV(1-1')\frac{\delta G(1,1'^+)}{\delta U(2)}+i\int d3\,d3'V(1-3)\frac{\delta G(1,3')}{\delta U(2)}\frac{\delta\Sigma(3',1')}{\delta U(3)}\\&\quad+i\int d3\,d3'V(1,3)G(1-3')\frac{\delta^2\Sigma(3',1')}{\delta U(2)\,\delta U(3)}.\end{aligned} \tag{62}$$

D. The Bethe–Salpeter Equation—Another Hierarchy of Equations

For purposes of physical insight and ease of derivation of exact cross-section expressions, a third form of the hierarchy will now be derived. This third form, which is equivalent to the previous two forms stresses the "optical" potentials. Closed equations shall be given for each Green's function. The unknown part of each equation will be an effective potential that requires a knowledge of higher Green's functions or equivalently higher functional derivatives of Σ.

The first equation of the hierarchy is again (48″) whose effective potential nature has already been discussed.

The second equation is obtained by replacing G_2 by a more convenient functional variable called the generalized linear response function and defined as

$$R(121'2')=\left.\frac{\delta G(1,1';U)}{\delta U(2',2)}\right|_{U=0}. \tag{63}$$

It is a generalized linear response because it is the coefficient of the linear term in the expansion of $G_1(1,1';U)$ in a power series in $U(2,2')$. For small U, it is the most important term describing the effect U has on the system.

The usual linear response is a special case of (63) and is (recalling that $1'^+\equiv\mathbf{r}_1', t_1+\varepsilon$)

$$R(121'^+2^+)=\left.\frac{\delta G_1(1,1'^+;U)}{\delta U(2^+,2)}\right|_{U=0}=i\frac{\delta\rho(1,1')}{\delta U(2)} \tag{64}$$

Therefore (64) gives the linear term in the expansion of the density matrix in a local potential. Comparing (56) and (63), it is clear that for a given G_1, R and G_2 give equivalent information, i.e.,

$$R(121'2') = -G_2(1, 2; 1', 2') + G_1(1, 1')G_1(2, 2') \tag{65}$$

To obtain a closed equation for R, Eq. (59) is combined with (63) and $\delta\Sigma/\delta U$ is replaced, using

$$\frac{\delta\Sigma(2, 3)}{\delta U(4, 5)} = \int d6\, d7\, \frac{\delta\Sigma(2, 3)}{\delta G_1(6, 7)} \frac{\delta G_1(6, 7)}{\delta U(4, 5)}$$

$$= \int d6\, d7 \Xi(2736)R(6574). \tag{66}$$

In the last step (63) has been used and the new definition

$$\Xi(2736) = \frac{\delta\Sigma(2, 3)}{\delta G_1(6, 7)} \tag{67}$$

has been introduced. The result is, after some changes of dummy integration variables, the *Bethe–Salpeter equation*

$$R(121'2') = G_1(1, 2')G_1(2, 1') + \int d3\, d3'\, d4\, d4' G_1(1, 3)G_1(3', 1')\Xi(343'4')R(4'242'). \tag{68}$$

Equation (68) is a closed equation for R (or G_2), which when compared to Eq. (48‴) shows that it is an integral equation for R describing the motion of two "Dyson" or "dressed" particles[15] [i.e., particles traveling in solutions of (48″)]—this is evident since G_1 and not G_1^0 is the unperturbed part of (68)—interacting via the effective media potential which already has removed from it the purely single particle effects. Of course, Ξ requires a knowledge of $\delta\Sigma/\delta G_1$, which can be shown to be equivalent to a knowledge of G_3 or higher functional derivatives of Σ with respect to U. Similar closed equations for higher Green's functions can be derived for dressed particles in the media. These shall not be needed here and shall be left out. The Dyson equation, (68) (called the Bethe–Salpeter equation) and the other effective potential equations form our last hierarchy.[16]

As in the case of the Dyson equation, solution of Eq. (68) is facilitated by deriving an equation for the spectral amplitude which has fewer variables. The property of (68) that t_2 and t_2' are parametric is very useful for such a derivation. Changing the parametric time variable to

$$\tau_2 = t_2 - t_2'$$

$$t^2 = \tfrac{1}{2}(t_2 + t_2') \qquad dt_2\, dt_2' = d\tau_2\, dt_2'.$$

[15] Note that a Dyson particle can be a particle or a hole.

[16] The usual form of the Bethe–Salpeter equation that appears in the literature involves G_2 and not R and is derived in Appendix B.

Equation (68) can be written as

$$R(1, 1', \mathbf{r}_2, \mathbf{r}_2', t^2, \tau_2) = R_0(1, 1', \mathbf{r}_2, \mathbf{r}_2', t^2, \tau_2) + \int d3\, d3'\, d4\, d4' R_0(13'1'3)\Xi(343'4')R(4', 4, \mathbf{r}_2, \mathbf{r}_2', t^2, \tau_2) \tag{69a}$$

where

$$R_0(121'2') = G_1(1, 2')G_1(2, 1'). \tag{69b}$$

Now, Fourier transforming with respect to $(-t^2)$ gives

$$R(1, 1', \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon) = R_0(1, 1', \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon) + \int d3\, d3'\, d4\, d4' R_0(13'1'3)\Xi(343'4')R(4', 4, \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon). \tag{70}$$

Since for the purposes of this review, only hole–particle amplitudes are of interest, further details will only be done for the hole-particle part of R, i.e., R^{hp}. The expression for R^{hp} in terms of the amplitudes is from (65) exactly that for G_2^{hp} given in (40d) except for an overall sign change (from "+" to "−") and the $n = 0$ term is removed from the summations (it is cancelled by the G_1G_1 term). Since the Fourier transform of G_2 has been given in (40e), the Fourier transform of R can be obtained exactly as (40a) and (40b) were obtained. Simply noting from Eq. (38b) that

$$R^{hp}(121'2') = \sum_{\omega_n \neq 0} e^{i\omega_n t^2} X_n(1, 1')\bar{X}_n(\mathbf{r}_2, \mathbf{r}_2; \tau_2)$$

and then proceeding exactly as in going from Eq. (38) to (40d) gives

$$R^{hp}(1, 1', \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon) = \lim_{\eta \to +0} i \sum_{\omega_n \neq 0} \frac{X_n(1, 1')\bar{X}_n(\mathbf{r}_2, \mathbf{r}_2'; \tau_2)\,\mathrm{sgn}(\omega_n)}{\varepsilon - \omega_n - i\eta\,\mathrm{sgn}(\omega_n)} \times \exp\left\{-\frac{i}{2}\mathrm{sgn}(\omega_n)[\varepsilon - \omega_n][|\tau_1| + |\tau_2|]\right\}. \tag{71}$$

Exactly as (38) compared to (40e), one obtains

$$R(1, 1', \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon) = R^{hp}(1, 1', \mathbf{r}_2, \mathbf{r}_2', \tau_2, \varepsilon) + \text{non-hole–particle terms with poles not at } \omega_n. \tag{72}$$

Substituting (72) into (70) and comparing the nth residues on both sides of the resulting equation and multiplying by $\varepsilon - \omega_n - i\eta\,\mathrm{sgn}(\omega_n)$, and taking the limit $\varepsilon \to \omega_n$ gives, after the common factor $\chi_n(\tau_2)$ is canceled,

$$X_n(1, 1') = \int d3\, d3'\, d4\, d4' R_0(13'1'3)\Xi(343'4')X_n(4', 4). \tag{73}$$

Equation (73) is the desired equation for the Bethe–Salpeter amplitude. It has been assumed the R_0 has no poles at ω_n. This is clearly not true for scattering states and hence (73) is a bound-state equation. However, as was previously discussed in connection with solving the Feynman–Dyson equation, for atomic and molecular problems one can span the relevant region of space with a discrete basis set. Within such a discrete basis the assumption holds and (73) can be used for the X's necessary to evaluate R.

Equation (73), the Bethe–Salpeter amplitude equation for bound states, is clearly a closed equation for the two-particle, hole–particle amplitude. Since R_0 depends on G_1 and not $G_1{}^0$, the hole and particle "move" in Dyson orbitals (the Dyson equation is assumed to be solved) and interact via Ξ which is the effective potential for hole–particle interactions of "dressed" particles and contains only true two-particle interactions with the single-particle average effects removed.

In order to obtain a Bethe–Salpeter equation valid for ω_n in the continuum, one must proceed slightly differently. Starting with the equation for R in terms of the X's where the (continuous) index is now integrated over

$$R(121'2') = \int d\omega_m X_m(1, 1')\bar{X}_m(2, 2')$$

multiply both sides by $X_n(2, 2')$ and integrate over 2 and 2'. It is not, in general, true that the X's are orthogonal, however, they have an exponential time dependence, Eq. (34), that goes as $e^{i\omega_n\tau}$. Since the times are integrated from $-\infty$ to $+\infty$ one obtains a $\delta(\omega_m - \omega_n)$ from the time integration. Hence,

$$X_n(1, 1') = \int d2\, d2' R(121'2')X_n(2, 2'), \tag{74}$$

where the X's are assumed to have already been normalized, and if there is any degeneracy that the X's within the degenerate set have been orthogonalized (which can always be done). Notice that Eq. (75) says that R is the two-particle kernel that propagates the two-particle amplitude X_n from space time points $\{\mathbf{r}_2 t_2, \mathbf{r}_2' t_2'\}$ to $\{\mathbf{r}_1 t_1, \mathbf{r}_1' t_1'\}$. Now substituting (68) into (74) and then again using (74) in the resulting equation gives

$$\begin{aligned} X_n(1, 1') = &\int d2\, d2' G_1(1, 2')G_1(2, 1')X_n(2, 2') \\ &+ \int d3\, d3'\, d4\, d4' G_1(1, 3)G_1(3', 1')\Xi(343'4')X_n(4', 4) \end{aligned} \tag{75}$$

which is the Bethe–Salpeter amplitude equation for continuum states, i.e., unbound hole–particle pairs. Note that it is of the same form as the bound state equation (73) except that it has an additional inhomogeneous term on the right-hand side. In Section IV we will elaborate this inhomogeneous term.

A similar equation could have been derived for hole–hole or particle–particle amplitudes. The two-particle Green's function G_2 would have been used and the terms in Eq. (39) with the proper poles stressed. An equation exactly like (73) would result except that X_n would be a hole–hole or particle–particle two-particle amplitude, and Ξ would be replaced by W (see Appendix B). These equations will not be stressed in this review since they do not, as discussed in Section II, lead to excitation energies.

In summary, three equivalent forms of the hierarchy of equations have been derived in this section: (*i*) that for G_1 related to G_2, G_2 to G_3, etc.; (*ii*) that for G_1 related to Σ, Σ to $\delta\Sigma$, $\delta\Sigma$ to $\delta^2\Sigma$ and $(\delta\Sigma)^2$, etc.; and (*iii*) that for G_1 given by a closed equation with a potential Σ, which requires a knowledge of R (or G_2) and a closed equation for R in terms of a potential Ξ, which depends on G_3 or higher variations in Σ.

Much time has been spent in obtaining various useful equivalent forms of the hierarchy-equations.

IV. Scattering[17]

The formulas and equations for scattering are here further developed using the exact relations of the previous section.

First the case of *elastic scattering* is considered. The purpose is to give a simple prescription for calculating the T matrix when Σ is given in exact, or approximate, form. The S matrix has already been given in Eq. (22) in terms of G. Here it shall be expressed in terms of solutions of (51) with proper elastic outgoing boundary conditions. It is here assumed that Σ has already been solved for exactly, or, on a finite basis set, approximately. To do this consider the one-particle amplitude that corresponds to the boundary conditions of an "in" or "out" elastic scattering experiment, i.e., the one related to $\Psi_{\mathbf{k}}{}^{\pm}$. This amplitude is, from Equation (26a),

$$f_{\mathbf{k}}^{(\pm)}(\mathbf{r}t) = \langle \Psi_0(N)|\psi(\mathbf{r}t)|\Psi_{\mathbf{k}}{}^{\pm}(N+1)\rangle. \tag{76}$$

Using (21), the inverse of (20), and inserting T since the limit already specifies the ordering, gives

$$\begin{aligned} f_{\mathbf{k}}^{(+)}(\mathbf{r}t) &= \lim_{t'\to-\infty} \langle \Psi_0|\psi(\mathbf{r}t)a_{\mathbf{k}}{}^{\dagger}(t')|\Psi_0\rangle \\ &= \lim_{t'\to-\infty} \int d\mathbf{r}' \langle T\psi(\mathbf{r}t)\psi^{\dagger}(\mathbf{r}'t')\rangle \varphi_{\mathbf{k}}(\mathbf{r}'t') \\ &= \lim_{t'\to-\infty} i\int d\mathbf{r}' G_1(\mathbf{r}t, \mathbf{r}'t')\varphi_{\mathbf{k}}(\mathbf{r}'t') \end{aligned} \tag{77}$$

where it is recalled that $\varphi_{\mathbf{k}}$ is a free-particle function.

[17] See Klein (1956), Klein and Zemach (1957), Bell and Squires (1959), Namiki (1960), Fetter and Watson (1965), Janev *et al.* (1969), and Csanak *et al.* (1971).

Putting (77) into (22) gives for the "+" case

$$S_{k'k} = \lim_{t' \to -\infty} \int d\mathbf{r}' \varphi_{k'}^*(1') f_k^{(+)}(1'). \tag{78}$$

Therefore a knowledge of $f_k^+(\mathbf{r}'\, t)$ gives $S_{k',k}$. Substituting (48‴) into (77) and using (77) again the expression for $f_k^{(+)}$ becomes

$$f_k^{(+)}(\mathbf{r}t) = \lim_{t' \to -\infty} \left\{ \int d\mathbf{r}' G_0(\mathbf{r}t, \mathbf{r}'t') \varphi_k(\mathbf{r}'t') + \int d\mathbf{r}_1\, dt_1\, d\mathbf{r}_2\, dt_2\, G_0(\mathbf{r}t, \mathbf{r}_1 t_1) \Sigma(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) G_1(\mathbf{r}_2 t_2, \mathbf{r}'t') \varphi_k(\mathbf{r}'t') \right\}$$

$$= \varphi_k(\mathbf{r}, t) + \int d\mathbf{r}_1\, dt_1\, d\mathbf{r}_2\, dt_2\, G_0(\mathbf{r}t, \mathbf{r}_1 t_1) \Sigma(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) f_k^{(+)}(\mathbf{r}_2 t_2). \tag{79}$$

It is now necessary to Fourier transform Eq. (79). To do this, time homogeneity is invoked to give

$$\Sigma(1, 1') = \Sigma(\mathbf{r}, \mathbf{r}'; t - t')$$

and the fact that $f_q^{(+)}(\mathbf{r}, t)$ can be rewritten as

$$f_q^{(+)}(\mathbf{r}t) = \langle \Psi_0{}^N | \psi(\mathbf{r}t) | \Psi_q^{+(N+1)} \rangle = \langle \Psi_0{}^N | e^{iHt} \psi(\mathbf{r}) e^{-iHt} | \Psi_q^{+(N+1)} \rangle$$
$$= \exp\left[-i(E_q^{N+1} - E_0{}^N)t\right] \langle \Psi_0{}^N | \psi(\mathbf{r}) | \Psi_q^{+(N+1)} \rangle$$
$$\equiv e^{-i\varepsilon_q t} f_q^{(+)}(\mathbf{r})$$

where

$$\varepsilon_q = E_q^{N+1} - E_0{}^N \qquad f_q^{(+)}(\mathbf{r}) = \langle \Psi_0{}^N | \psi(\mathbf{r}) | \Psi_q^{+(N+1)} \rangle$$

to give from Eq. (79)

$$f_q^{(+)}(\mathbf{r}) e^{-i\varepsilon_q t} = \varphi_q(\mathbf{r}) e^{-i\varepsilon_q t} + \int d\mathbf{r}_1 dt_1 d\mathbf{r}_2\, dt_2\, G_0(\mathbf{r}, \mathbf{r}_1; t - t_1) \Sigma(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) f_q^{(+)}(\mathbf{r}_2) e^{-i\varepsilon_q t_2}. \tag{79'}$$

Letting

$$\tau = t - t_1 \qquad \tau_1 = t_1 - t_2 \qquad dt_1\, dt_2 = d\tau\, d\tau_1$$

multiplying through by $e^{i\varepsilon_q t}$, and integrating τ_1 and τ_2, using the standard Fourier transform definitions, gives

$$f_q^{(+)}(\mathbf{r}) = \varphi_q(\mathbf{r}) + \lim_{\eta \to +0} \int G_0(\mathbf{r}, \mathbf{r}_1; \varepsilon_q + i\eta) \Sigma(\mathbf{r}, \mathbf{r}_2; \varepsilon_q) f_q^{(+)}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{79''}$$

where the $i\eta$ is added because, since $t \to +\infty$, τ is positive, which requires that the inverse transform of $G_0(\varepsilon)$ be done by closing the contour in the lower half plane. The "$i\eta$" guarantees, by the residue theorem, that nonzero solutions only occur when the contour is closed properly, and that Eq. (79″) has the proper boundary conditions.

Equation (79″) is the integral form of (51′) with the elastic "out-going scattering wave," "incoming free wave" boundary conditions built in. It shows that $f_k^{(+)}$ is a solution of Eq. (51) for a given energy $\varepsilon_k = k^2/2$ and with outgoing boundary conditions. Hence, if Σ is solved for in any way, the solution of the elastic scattering problem is exactly the same as a nonlocal potential problem, for which many methods are known (Reinhardt and Szabo, 1970), the determinental method being especially appropriate. In deriving Eq. (79) the integral without Σ was replaced by φ_k, the plane wave. To see the correctness of this procedure, note that

$$\lim_{t' \to -\infty} \int d\mathbf{r}' G_0(\mathbf{r}t, \mathbf{r}'t') \varphi_k(\mathbf{r}'t')$$
$$= \lim_{t' \to -\infty} \int d\mathbf{r}' \langle \Psi_0{}^0 | \psi_0(\mathbf{r}t) \psi_0{}^\dagger(\mathbf{r}'t') | \Psi_0{}^0 \rangle \varphi_k(\mathbf{r}'t')$$
$$= \lim_{t' \to -\infty} \langle \Psi_0{}^0 | \psi_0(\mathbf{r}t) a_k{}^\dagger(t') | \Psi_0{}^0 \rangle = \langle \Psi_0{}^0 | \psi_0(\mathbf{r}t) | \Psi_k^{0+} \rangle.$$

Here the new "0" indicates "unperturbed" and $\langle \Psi_0{}^0 | \psi_0 | \Psi_k^{0+} \rangle$ is clearly the free-particle one-particle amplitude, which by the Dyson equation, since Σ is here zero, is just an incoming plane wave.

It is now convenient to have a T matrix form and then to convert from time variables to energy variables. To this end, if Eq. (79) is substituted into (81) and the analog for (27) is used for G_0,

$$G_0(\mathbf{r}t, \mathbf{r}'t') = \frac{1}{i} \sum_j \varphi_j(\mathbf{r}t) \varphi_j{}^*(\mathbf{r}'\, t') \qquad \text{for} \quad t > t'$$

the equation for $S_{kk'}$ becomes

$$S_{k'k} = \lim_{t' \to +\infty} \left\{ \int d\mathbf{r}' \varphi_k(\mathbf{r}'t') \varphi_{k'}^*(\mathbf{r}'t') + \sum_j \frac{1}{i} \int d\mathbf{r}' \varphi_j(\mathbf{r}'t') \varphi_{k'}^*(\mathbf{r}'t') \int d\mathbf{r}\, dt\, d\mathbf{r}''\, dt'' \varphi_j{}^*(\mathbf{r}t) \Sigma(\mathbf{r}t, \mathbf{r}''t'') f_k^{(+)}(\mathbf{r}''t'') \right\}.$$

Using the conservation of energy and momentum in the form

$$\lim_{t' \to +\infty} \int d\mathbf{r}' \varphi_j(\mathbf{r}'t') \varphi_p{}^*(\mathbf{r}'t') = \lim_{t' \to +\infty} e^{i(\varepsilon_p - \varepsilon_j)t'} \int d\mathbf{r}' \varphi_j(\mathbf{r}') \varphi_p{}^*(\mathbf{r})$$
$$= \delta(\varepsilon_p - \varepsilon_j) \delta_{jp}$$

gives

$$S_{k'k} = \delta(\varepsilon_k - \varepsilon_{k'})\left\{\delta_{kk'} + \frac{1}{i}\int d\mathbf{r}'\, dt'\, d\mathbf{r}''\, dt''\varphi_{k'}^*(\mathbf{r}'t')\Sigma(\mathbf{r}'t', \mathbf{r}''t'')f_k^{(+)}(\mathbf{r}''t'')\right\}. \quad (80a)$$

Now defining T by the standard relation

$$S = 1 + T$$

gives

$$T_{k'k} = \frac{1}{i}\int d1\; d1'\varphi_{k'}^*(1)\Sigma(1, 1')f_k^{(+)}(1'). \quad (80b)$$

Note that T has the advantage over S that the limiting process which is difficult to perform is eliminated. To express the T matrix in terms of $f_k(\mathbf{r})$, (80b) is written as

$$T_{pq} = \frac{1}{i}\int d1'\; d1''\varphi_p^*(\mathbf{r})\, e^{it\varepsilon_p t'}\Sigma(\mathbf{r}', \mathbf{r}''; t' - t'')f_q^{(+)}(\mathbf{r}'')\, e^{-it\varepsilon_q t''}$$

$$= \frac{1}{i}\int d\mathbf{r}'\, d\mathbf{r}''\varphi_p^*(\mathbf{r}')\int d\tau\Sigma(\mathbf{r}', \mathbf{r}''; \tau)\, e^{it\varepsilon_p\tau}\int dt''\, e^{i(\varepsilon_p - \varepsilon_q)t''}f_q^{(+)}(\mathbf{r}'')$$

$$= \delta(\varepsilon_p - \varepsilon_q)\frac{2\pi}{i}\int d\mathbf{r}\, d\mathbf{r}'\varphi_p^*(\mathbf{r})\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_p)f_q^{(+)}(\mathbf{r}'). \quad (81)$$

Equation (81) is what shall be used in practice since $\Sigma(\varepsilon_p)$ and $f_q^{(+)}(\mathbf{r}')$ is what is usually available when time-independent methods (which are easier to work with) are used.

The next equation to be derived is for *inelastic scattering*. Analogous to the derivation of Eq. (21), the expression for the S matrix element for a scattering process that excites the target from state 0 to state n with electron initial and final momentum $\mathbf{p}$ and $\mathbf{q}$, respectively, is

$$S_{0p,nq} = \langle\Psi_{0p}^{-(N+1)}|\Psi_{nq}^{+(N+1)}\rangle = \lim_{\substack{t'\to+\infty\\ t\to-\infty}}\langle\Psi_0{}^N|a_p(t')a_q^\dagger(t)|\Psi_n{}^N\rangle$$

$$= \lim_{\substack{t'\to+\infty\\ t\to-\infty}}\int d\mathbf{r}\, d\mathbf{r}'\varphi_p^*(\mathbf{r}'t')\chi_n(1', 1)\varphi_q(\mathbf{r}t). \quad (82)$$

It is evident that the two-particle, hole-particle amplitude is needed here, which requires a knowledge of Ξ (or G_3). An alternative viewpoint comes from a comparison of the definitions of G_1 and χ_n, which shows that χ_n is reasonably considered an "off diagonal one-particle Green's function," and should be related to off diagonal optical potentials and responses. If the bound state Bethe–Salpeter equation for hole-particle amplitudes (73) is substituted into Eq. (82), another form, which is possibly more useful for making approximations, is obtained.

$$S_{0p,nq} = \frac{1}{i^2}\int d1\; d2\; d3\; d4\, f_p^{(-)*}(1)\Xi(1423)\chi_n(3, 4)f_q^{(+)}(2) \quad (83)$$

where the f's are special solutions of the ground state Dyson equation defined by

$$f_q^{(+)}(2) = \lim_{t_2'\to-\infty} i\int d\mathbf{r}_2'\varphi_q(2')G(2, 2')$$

$$f_q^{(-)*}(1) = \lim_{t_1'\to\infty} i\int d\mathbf{r}_1'G(1'1)\varphi_q^*(1'). \quad (84)$$

The time independent form of Eq. (83) showing the proper energy conservation is obtained by substituting Eq. (79′) and (34) into (83), with the changes of variables

$$\tau = t_3 - t_4 \qquad t = \tfrac{1}{2}(t_3 + t_4); \qquad \mu = t_1 - t_2$$

$$s = \tfrac{1}{2}(t_1 + t_2) \qquad \sigma = s - t; \qquad \omega_n = E_n - E_0$$

to obtain

$$S_{0p,nq} = \frac{1}{i^2}\int d\sigma\, dt\, d\mu\, d\tau\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 f_p^{(-)*}(\mathbf{r}_1)f_q^{(+)}(\mathbf{r}_2)$$

$$\times\, e^{i(\varepsilon_p - \varepsilon_q)\sigma}\, e^{i(\varepsilon_p - \varepsilon_q - \omega_n)t}\, e^{i(\varepsilon_p + \varepsilon_q)\mu/2}\Xi(\mathbf{r}_1\mathbf{r}_4\mathbf{r}_2\mathbf{r}_3\mu\tau\sigma)\chi_n(\mathbf{r}_3, \mathbf{r}_4, \tau).$$

Integration over t gives the energy conserving δ-functions. Integration over σ and μ Fourier transforms $\Xi(\mu, \tau, \sigma)$ to $\Xi[(\varepsilon_p + \varepsilon_q)/2, \tau, \varepsilon_p - \varepsilon_q]$ integration over τ after substituting in the Fourier integral representations of $\Xi(\tau)$ and $\chi(\tau)$ gives finally

$$S_{0p,nq} = \frac{1}{i^2}\delta(\varepsilon_p - \varepsilon_q - \omega_n)\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 f_p^{(-)*}(\mathbf{r}_1)f_q^{(+)}(\mathbf{r}_2)\int d\varepsilon$$

$$\times\,\Xi\left(\mathbf{r}_1\mathbf{r}_4\mathbf{r}_2\mathbf{r}_3, \frac{\varepsilon_p + \varepsilon_q}{2}, -\varepsilon, \varepsilon_p - \varepsilon_q\right)\chi_n(\mathbf{r}_3\mathbf{r}_4\varepsilon) \quad (85)$$

If Ξ is known (e.g., by solving for it perturbationally by the method to be discussed in Section VI, D) then the inelastic electron scattering cross section can be evaluated from Eq. (85).

The equation for inelastic scattering of an electron off a target, since it only uses electron amplitudes for a ground state target [see, Eq. (84)], has a somewhat strange appearance. The more usual description of inelastic scattering as in Eq. (82) has the electron leaving the target with the target in its excited state. It is just this necessity of describing the system in terms of its excited state wavefunction that the Bethe–Salpeter amplitude equation does away with. That is, the excited state wavefunction is considered to have been

created adiabatically from an excitation of the ground state system, this process will be described in detail below for a somewhat different case. If one recalls the derivation of the Bethe–Salpeter amplitude equation in Section III, where one starts with an equation for R in terms of an $X\tilde{X}$ product, one sees that this is exactly analogous to the process of obtaining excited state information such as oscillator strengths by looking at the poles and residues of a ground state property, the frequency dependent polarizability. There, one obtains inelastic photon scattering information, the absorption oscillator strength, by using the polarizability, whose defining equation involves only ground state quantities.

To complete the scattering picture, formulas for χ_n are needed when ω_n is greater than the ionization potential. Here χ_n is a continuum function and R_0 has poles (or rather a cut) at ω_n, so that the bound state Bethe–Salpeter equation no longer holds. Special continuum χ_n are needed if exact R or G_2 are to be calculated and the discrete basis approximation not made. A second reason for calculating the continuum χ_n is that it obviously contains information about the ionization continuum of the target. From this information it should be possible to obtain information about scattering from the ion. To do this it is necessary to study the effect of adiabatic decoupling on the electrons of the target atom itself. The ground state and some specific states of the ion can be described in the independent particle model as a hole in the ground state of the atom.

$$|\Phi_m\rangle = \tilde{a}_m|\Phi_0\rangle$$

where $|\Phi_0\rangle$ is the ground state in this approximation and m is a quantum number referring to a ground state occupied orbital. In the following the Hartree–Fock independent particle model is used and $\tilde{a}_m$ creates a Hartree–Fock hole. Also the field operator is

$$\psi(\mathbf{r}) = \sum_n \tilde{a}_n \varphi_n^{\mathrm{HF}}(\mathbf{r}).$$

The Heisenberg operator is expressed as

$$\psi(\mathbf{r}\,t) = \sum_n \tilde{a}_n(t)\varphi_n^{\mathrm{HF}}(\mathbf{r}\,t)$$

where $\varphi_n^{\mathrm{HF}}(\mathbf{r})$ and $\varphi_n^{\mathrm{HF}}(\mathbf{r}\,t)$ are the Hartree–Fock orbitals for the time independent and a freely propagating time dependent case, respectively. $\tilde{a}_m(t)$ is neither a pure Heisenberg nor interaction operator, but is a mixed representation. It is defined by the equation for $\psi(\mathbf{r})$ and $\psi(\mathbf{r}\,t)$ which are related by the usual Heisenberg transform. The tilde on the $\tilde{a}_m$ simply distinguishes it from that for free (neutral targets) or Coulomb (charged target) waves. Now starting from the uncoupled state, by adiabatically turning on of the correlation potential, an exact ion state can be reached:

$$|\Psi_m\rangle = \tilde{a}_m^{\mathrm{in}}|\Psi_0\rangle$$

where

$$\tilde{a}_m^{\mathrm{in}} = \lim_{t\to-\infty} \tilde{a}_m(t).$$

This $|\Psi_m\rangle$ will be used as an ionic target state in the formalism used previously for electron-atom scattering. In this case, the scattering matrix assumes the form:

$$\begin{aligned} S_{\mathbf{p}m_1,\mathbf{q}m_2} &= \langle\Psi^-_{\mathbf{p}m_1}|\Psi^+_{\mathbf{q}m_2}\rangle = \langle\Psi_{m_1}|a_{\mathbf{p}}^{\mathrm{out}}a_{\mathbf{q}}^{\dagger\mathrm{in}}|\Psi_{m_2}\rangle \\ &= \lim_{\substack{t_1t_2\to-\infty\\ t_1't_2'\to+\infty}} \langle a_{\mathbf{p}}(t_1')\tilde{a}^{\dagger}_{m_1}(t_2')a^{\dagger}_{\mathbf{q}}(t_1)\tilde{a}_{m_2}(t_2)\rangle \\ &= \lim_{\substack{t_1t_2\to-\infty\\ t_1't_2'\to+\infty}} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_1'\, d\mathbf{r}_2'\; G(\mathbf{r}_1't_1', \mathbf{r}_2t_2\,;\, \mathbf{r}_1t_1, \mathbf{r}_2't_2') \\ &\quad\times \varphi_{\mathbf{p}}{}^*(\mathbf{r}_1't_1')\varphi^{\mathrm{HF}}_{m_1}(\mathbf{r}_2't_2')\varphi_{\mathbf{q}}(\mathbf{r}_1t_1)\varphi^{\mathrm{HF}*}_{m_2}(\mathbf{r}_2t_2) \end{aligned} \tag{86}$$

where $\varphi_{\mathbf{p}}(\mathbf{r}t)$, $\varphi_{\mathbf{q}}(\mathbf{r}t)$ are Coulomb waves whereas $\varphi^{\mathrm{HF}}_{m_1}(\mathbf{r}t)$, $\varphi^{\mathrm{HF}}_{m_2}(\mathbf{r}t)$ are Hartree–Fock one-particle stationary states (m_1, m_2 are Hartree–Fock quantum numbers). The change here from the electron-atom scattering case is that the indices $\mathbf{p}$ and $\mathbf{q}$ refer to Coulomb wavenumbers and $\varphi_{\mathbf{p}}(\mathbf{r}t)$ and $\varphi_{\mathbf{q}}(\mathbf{r}t)$ are Coulomb functions. The use of Coulomb functions is conditioned by the long range electron–ion interaction. The scattering matrix formula can be simplified by defining the Bethe–Salpeter amplitude referring to the state $|\Psi^+_{\mathbf{q}m}\rangle$:

$$\begin{aligned} \chi^{(+)}_{\mathbf{q}m_1}(1,2) &= \langle\Psi_0|T[\psi(1)\psi^{\dagger}(2)]|\Psi^+_{\mathbf{q}m_1}\rangle \\ &= \lim_{t,t'\to-\infty} \langle\Psi_0|T[\psi(1)\psi^{\dagger}(2)]\tilde{a}_{m_1}(t)a^{\dagger}_{\mathbf{q}}(t')|\Psi_0\rangle \\ &= \lim_{t,t'\to-\infty} \int d\mathbf{r}\, d\mathbf{r}'\, \langle T[\psi(1)\psi^{\dagger}(2)\psi(\mathbf{r}t)\psi^{\dagger}(\mathbf{r}'t')]\rangle\, \varphi_{\mathbf{q}}(\mathbf{r}'t')\varphi^{\mathrm{HF}*}_{m_1}(\mathbf{r}t) \\ &= \lim_{\substack{t\to-\infty\\ t'+\varepsilon\to-\infty}} (-1)\int d\mathbf{r}\, d\mathbf{r}'\, G_2(1,\mathbf{r}t;\,2,\mathbf{r}'t')\varphi_{\mathbf{q}}(\mathbf{r}'t')\varphi^{\mathrm{HF}*}_{m_1}(\mathbf{r}t) \end{aligned} \tag{87}$$

Using this expression in the scattering matrix formula, it becomes

$$S_{\mathbf{p}m_1,\mathbf{q}m_2} = \lim_{t_1't_2'\to-\infty} \int d\mathbf{r}_1'd\mathbf{r}_2'\; \varphi_{\mathbf{p}}{}^*(\mathbf{r}_1't_1')\varphi^{\mathrm{HF}}_{m_1}(\mathbf{r}_2't_2')\chi^{(+)}_{\mathbf{q}m_2}(\mathbf{r}_1't_1', \mathbf{r}_2't_2'). \tag{88}$$

From the Bethe–Salpeter equation, an inhomogeneous (nonlinear) integral equation can be derived for the $\chi^{(+)}_{\mathbf{q}m_2}(1,2)$ Bethe–Salpeter amplitude.

Inserting (65) and (68) into (88) and using the following identities

$$\lim_{\substack{t\to-\infty\\ t'+\varepsilon\to-\infty}} \int d\mathbf{r}\, d\mathbf{r}'\, G(1,1')\varphi_{\mathbf{q}}(1')\varphi_m^{\mathrm{HF}*}(1)$$

$$= \lim_{\substack{t\to-\infty\\ t'+\varepsilon\to-\infty}} \int d\mathbf{r}\, d\mathbf{r}'\, \langle\psi(1)\psi^{\dagger}(1')\rangle\varphi_{\mathbf{q}}(1')\varphi_m^{*}(1)$$

$$= \lim_{\substack{t\to-\infty\\ t'+\varepsilon\to-\infty}} \langle a_m(t)a_{\mathbf{q}}^{\dagger}(t')\rangle = \langle\Psi_0|\Psi_{\mathbf{q}m}^{(+)}\rangle = 0$$

and

$$\lim_{t'\to-\infty} i\int d\mathbf{r}_1'\, G(1,1')\varphi_{\mathbf{q}}(1') = f_{\mathbf{q}}^{(+)}(1)$$

$$\lim_{t_1\to-\infty} i\int d\mathbf{r}_1\, G(1,2)\varphi_m^{\mathrm{HF}*}(1) = -g_m^{*}(2)$$

the following equation is obtained for the Bethe–Salpeter amplitude

$$\chi_{\mathbf{q}m}^{(+)}(1,2) = f_{\mathbf{q}}^{(+)}(1)g_m^{*}(2) + \int d3\, d3'\, d4\, d4'\, R_0(1423)\Xi(34'43')\chi_{\mathbf{q}m}^{(+)}(3',4') \tag{89}$$

where $f_{\mathbf{q}}(1)$ is the solution of the Dyson equation with incoming Coulomb wave of wave vector $\mathbf{q}$ boundary condition and $g_m(2)$ is the solution of the Dyson equation with Hartree–Fock boundary conditions

$$g_n(2) = \varphi_n^{\mathrm{HF}}(2) + \int d3d4G_{\mathrm{HF}}(2,3)\Sigma_{\mathrm{corr}}(3,4)g_n(4) \tag{90}$$

where $G_{\mathrm{HF}}(2,3)$ is the Hartree–Fock one-particle Green's function and $\Sigma_{\mathrm{corr}} = \Sigma - \Sigma_{\mathrm{HF}}$ where Σ_{HF} is the Hartree–Fock potential. This equation follows from the following form of the Dyson equation

$$G = G_{\mathrm{HF}} + G_{\mathrm{HF}}\Sigma_{\mathrm{corr}}G.$$

Now, the substitution of $\chi_{\mathbf{q}m_2}^{(+)}$ from Eq. (89) to the scattering matrix expression given by Equation (88) gives

$$S_{\mathbf{p}m_1,\mathbf{q}m_2} = \lim_{t_1'\to\infty}\int d\mathbf{r}_1'\,\varphi_{\mathbf{p}}^{*}(\mathbf{r}_1't_1')f_{\mathbf{q}}^{(+)}(\mathbf{r}_1't_1')\lim_{t_2'\to\infty}\int d\mathbf{r}_2'\varphi_{m_1}^{\mathrm{HF}}(\mathbf{r}_2'\,t_2')$$
$$\times g_m^{*}(\mathbf{r}_2't_2') + \sum_{\mathbf{p}'}\sum_{m'}\lim_{t_1'\to\infty}\int d\mathbf{r}_1'\,\varphi_{\mathbf{p}}^{*}(\mathbf{r}_1't_1')f_{\mathbf{p}'}^{(+)}(\mathbf{r}_1't_1')$$
$$\times \lim_{t_2'\to\infty}\int d\mathbf{r}_2'\,\varphi_{m_1}^{\mathrm{HF}}(\mathbf{r}_2't_2')g_{m'}^{*}(\mathbf{r}_2't_2')\int d3\, d3'\, d4\, d4' f_{\mathbf{p}'}^{(+)*}(3)$$
$$\times g_{m'}(4)\Xi(34'43')\chi_{\mathbf{q}m_2}^{(+)}(3',4'). \tag{91}$$

This formula can be simplified noticing that

$$\lim_{t'\to\infty}\int d\mathbf{r}'\,\varphi_{\mathbf{p}}^{*}(\mathbf{r}'t')f_{\mathbf{p}'}(\mathbf{r}'t') = S_{\mathbf{p}\mathbf{p}'}. \tag{92}$$

The same expression occurred previously in the electron-atom scattering formula, however, $\mathbf{p}$ and $\mathbf{p}'$ here refer to Coulombic functions.

Similar expressions can be defined for the "hole scattering"

$$\lim_{t'\to\infty}\int d\mathbf{r}'\,\varphi_{m_1}^{\mathrm{HF}}(\mathbf{r}'t')g_{m'}(\mathbf{r}'t') = \tilde{S}_{m_1m'}. \tag{93}$$

Finally the following formula is obtained:

$$S_{\mathbf{p}m,\mathbf{q}m_2} = S_{\mathbf{p}\mathbf{q}}\tilde{S}_{m_1m_2} + \sum_{\mathbf{p}'}\sum_{m'}S_{\mathbf{p}\mathbf{p}'}\tilde{S}_{m_1m'}T_{\mathbf{p}'m',\mathbf{q}m_2} \tag{94}$$

where

$$T_{\mathbf{p}'m',\mathbf{q}m_2} = \int d3\, d3'\, d4\, d4'\, f_{\mathbf{p}'}^{(+)*}(3)g_{m'}(4)\Xi(34'43')\chi_{\mathbf{q}m_2}^{(+)}(3',4'). \tag{95}$$

The first term in Equation (94) describes the independent scattering of the particle and the hole, the second term expresses the interference of these scatterings.

The energy-dependent form of the T matrix in (94) is

$$T_{\mathbf{p}'m',\mathbf{q}m_2} = \delta(\varepsilon_{\mathbf{p}'} + \varepsilon_{m'} - \omega_{\mathbf{q}m_2})\int d\mathbf{r}_1\, d\mathbf{r}_1'\, d\mathbf{r}_2\, d\mathbf{r}_2'\, f_{\mathbf{p}'}^{(+)}(\mathbf{r}_1)g_{m'}^{*}(\mathbf{r}_2)2\pi\int d\varepsilon$$
$$\times\,\Xi\left(\mathbf{r}_1,\mathbf{r}_2',\mathbf{r}_2,\mathbf{r}_1',\frac{\varepsilon_{\mathbf{p}'}-\varepsilon_{m'}}{2},\varepsilon,\varepsilon_{\mathbf{p}'}-\varepsilon_{m'}\right)\chi_{\mathbf{q}m_2}^{(+)}(\mathbf{r}_1',\mathbf{r}_2'). \tag{96}$$

It is this form of the equation for the electron-ion T matrix which should prove most useful when combined with the perturbation expansion for Ξ, as given in Section VI.

The formula for the scattering matrix equation (94) can be made more symmetric. The equation for the Dyson orbital $f_{\mathbf{k}}^{(+)}(1)$:

$$f_{\mathbf{k}}^{(+)}(1) = \varphi_{\mathbf{k}}(1) + \int G_0(1,2)\Sigma(2,3)f_{\mathbf{k}}^{(+)}(3)\, d2\, d3 \tag{97}$$

can be solved in two steps. In the first step we construct the Hartree–Fock orbital $\varphi_{\mathbf{k}}^{\mathrm{HF}}(1)$ with outgoing Coulomb wave boundary condition:

$$\varphi_{\mathbf{k}}^{\mathrm{HF}}(1) = \varphi_{\mathbf{k}}(1) + \int G_0(1,2)\Sigma_{\mathrm{HF}}(2,3)\varphi_{\mathbf{k}}^{\mathrm{HF}}(3)\, d2\, d3 \tag{98}$$

and then solve the Dyson equation with $\Sigma_{\mathrm{corr}} = \Sigma - \Sigma_{\mathrm{HF}}$ using $\varphi_{\mathbf{k}}^{\mathrm{HF}}$ as the inhomogeneous term

$$f_k^{(+)}(1) = \varphi_k^{HF}(1) + \int G_{HF}(1, 2)\Sigma_{corr}(2, 3) f_k^{(+)}(3)\, d2\, d3. \tag{99}$$

S_{pq} can be written as

$$S_{pq} = \lim_{t_1' \to \infty} \int d\mathbf{r}_1'\, \varphi_p^*(\mathbf{r}_1' t_1') \varphi_q^{HF}(\mathbf{r}_1' t_1') + \lim_{t_1' \to \infty} \sum_r \int d\mathbf{r}_1'\, \varphi_r^{HF}(\mathbf{r}_1' t_1')$$
$$\times \varphi_p^*(\mathbf{r}_1' t_1') \int \varphi_r^{HF*}(2)\Sigma_{corr}(2, 3) f_q^{(+)}(3)\, d2\, d3. \tag{100}$$

In the eigenphase representation the Hartree–Fock scattering matrix is diagonal, therefore

$$\lim_{t_1' \to \infty} \int \varphi_r^{HF}(1') \varphi_p^*(1')\, d\mathbf{r}_1' = S(\mathbf{p})\, \delta_{rp} \tag{101}$$

and consequently

$$\begin{aligned} S_{pq} &= S(\mathbf{p})\, \delta_{pq} + \sum_r S(\mathbf{r})\, \delta_{rp}\, T_{rq} \\ &= S(\mathbf{p})\, \delta_{pq} + S(\mathbf{p}) T_{pq} \\ &= S(\mathbf{p}) \bar{S}_{pq}, \end{aligned} \tag{102}$$

where

$$T_{pq} = \int \varphi_p^{HF*}(2)\Sigma_{corr}(2, 3) f_q^{(+)}(3)\, d2\, d3 \tag{103}$$

and

$$\bar{S}_{pq} = \delta_{pq} + T_{pq}. \tag{104}$$

The substitution of the form of S_{pq} into (94) gives

$$\begin{aligned} S_{pm_1, qm_2} &= S(\mathbf{p}) \bar{S}_{pq} \tilde{S}_{m_1 m_2} + \sum_{p'} \sum_{m'} S(\mathbf{p}) \bar{S}_{pp'} \tilde{S}_{m_1 m'} T_{p'm', qm_2} \\ &= S(\mathbf{p}) \left\{ \bar{S}_{pq} \tilde{S}_{m_1 m_2} + \sum_{p'} \sum_{m'} \bar{S}_{pp'} \tilde{S}_{m_1 m'} T_{p'm', qm_2} \right\}. \end{aligned} \tag{105}$$

V. Nonperturbative Approximation Method[18]

Now that the formal equations are developed an "equation decoupling procedure" is needed to truncate any of the three equivalent sets of coupled equations of Section III. This approximation will also simplify the scattering formulae involving Ξ. The idea behind the approximation is to guess a

[18] See Dyson (1949); Feynman (1951); Matsubara (1955); Martin and Schwinger (1959); Baym and Kadanoff (1961); Schneider *et al.* (1970); Csanak *et al.* (1971),

functional form for Σ (the reason that the G_1, G_2, G_3, ... hierarchy was replaced by the two other equivalent ones which stressed functional derivatives, was to make Σ more visible). A "functional form" means a specified dependance of Σ on G_1, for unspecified G_1. Since this guess defines the model and will be used to generate the physics of the problem, it must be physically well motivated. Once this is done the hierarchy can be closed in any one of an infinite number of ways each of which gives a higher order self-consistent set of equations, viz.: If $\Sigma \approx \Sigma^A(G_1)$ is put into the Dyson equation, the system is truncated to one closed equation for G_1 requiring no other information. Since this equation is nonlinear it will be solved iteratively (or self-consistently). If, on the other hand, $\Sigma \approx \Sigma^A(G_1)$ is used in $\delta\Sigma \approx \delta\Sigma^A(G_1)$ with $\delta^n\Sigma \to 0$, for $n \geq 2$, a set of two coupled equations are obtained, namely the Dyson equation for G_1 in terms of Σ; a formula (not "eaqution") for Σ in terms of G_1, V, and R, and a closed equation for R in terms of G_1. There two coupled equations must be solved iteratively and hence self-consistently. If the approximation is made for higher functional derivatives, i.e., $\delta^n\Sigma/\delta U^n$, $n = 0, 1$ is unspecified but $\delta^2\Sigma \approx \delta^2\Sigma^A(G_1)$ with $\delta^n\Sigma/\delta U^n = 0$, $n = 3, 4, \ldots$ larger and higher self-consistent sets are defined. Hence, it is seen how higher and different types of self-consistencies can be developed. It is hoped (and moreover physically reasonable) that higher self-consistencies are better, since the model Σ^A is being used only to calculate smaller and smaller variations of Σ rather than Σ itself. This will be seen to be true explicitly in the context of perturbation theory in Section VI.

The problem now is to choose the form of $\Sigma^A(G_1)$; from the discussion above, especially with reference to the single equation truncation, the choice of $\Sigma_{HF}(G_1)$ as the Hartree–Fock functional form is suggested. In Section VI this will be shown to be the first-order perturbational approximation to $\Sigma(G)$. Now

$$\begin{aligned} \Sigma_{HF}(1, 1'; G_1) = \Sigma_{HF}(1, 1') &= -i\delta(1 - 1') \int d2V(1 - 2) G_1(2, 2^+) \\ &\quad + iV(1 - 1') G_1(1, 1'^+) \end{aligned} \tag{106}$$

because if G_1 is taken as G_{HF} (i.e., the Dyson orbitals and energies in the spectral representation of G_1 are taken as Hartree–Fock orbitals and energies) $\Sigma_{HF}(G_1)$ becomes the Hartree–Fock potential. Note that $\Sigma_{HF}(G_1)$ is generally not the Hartree–Fock potential since $G_1 \neq G_{1HF}$. If this approximation is made in the Dyson equation, the total theory reduces to the Hartree–Fock model which is unsatisfactory for anything except the ground state density and expectation values of one particle operators. The next step, and the contribution by Schneider *et al.*, (1970), is to do the second step, i.e., leave Σ alone but use

$$\delta\Sigma \to \delta\Sigma_{HF}. \tag{107}$$

With this, using Equation (67), the approximate form of Ξ is obtained

$$\Xi(343'4') = \frac{\delta\Sigma(3,3')}{\delta G_1(4',4)} \approx \frac{\delta\Sigma_{\mathrm{HF}}(3,3')}{\delta G_1(4',4)} = \Xi_A(343'4')$$
$$= i\delta(3-4')\delta(3'^{+}-4)V(3-3')$$
$$- i\delta(3-3')\delta(4-4'^{+})V(3-4'). \tag{108}$$

It will be shown in Section VI that Eq. (108) is the first-order term in the perturbation expansion of Ξ as a function of G.

Now inserting (108) into (73) gives

$$X_n(1,1') = -i\int d2\,d2' R_0(12'1'2)V(2-2')X_n(2'2'^{+})$$
$$+ i\int d2\,d2' R_0(12'1'2)V(2-2')X_n(22'^{+}). \tag{109}$$

Using the $\delta(t_2 - t_2')$ hidden in the definition of $V(2-2')$ shows that on the right-hand side of (109) the first and second terms contain, respectively, $X_n(\mathbf{r}_2', \mathbf{r}_2'; t^2, -0)$ and $X_n(\mathbf{r}_2, \mathbf{r}_2'; t^2, -0)$. Hence, in this approximation $X_n(1,1')$ is obtained from a knowledge of $X_n(\mathbf{r}_2, \mathbf{r}_2'; t^2, -0)$ and G_1. $X_n(\mathbf{r}_2, \mathbf{r}_2'; t^2, -0)$ is obtained from the closed equation obtained from (109) by choosing $t_1' = t_1 + \varepsilon$, so that $\{t_1, t_1'\} \to \{t' = t_1 = t_1', \tau_1 = -0\}$

$$X_n(\mathbf{r}_1, \mathbf{r}_1'; t', -0) = -i\int d\mathbf{r}_2\,d\mathbf{r}_2'\,dt^2 R_0(\mathbf{r}_1 t', \mathbf{r}_2 t^2, \mathbf{r}_1 t'^{+}, \mathbf{r}_2 t^2)$$
$$\times V(|\mathbf{r}_2 - \mathbf{r}_2'|)X_n(\mathbf{r}_2', \mathbf{r}_2', t^2, -0)$$
$$+ -i\int d\mathbf{r}_2\,d\mathbf{r}_2'\,dt^2 R_0(\mathbf{r}_1 t', \mathbf{r}_2 t^2, \mathbf{r}_1 t'^{+}, \mathbf{r}_2 t^2)$$
$$\times V(|\mathbf{r}_2 - \mathbf{r}_2'|)X_n(\mathbf{r}_2, \mathbf{r}_2', t^2, -0) \tag{110}$$

where from Eqs. (40c), (34), and (35)

$$X_n(\mathbf{r}_1, \mathbf{r}_1', t', -0) = \begin{cases} -e^{-i\omega_n t'}\langle \Psi_0^N | \psi^\dagger(\mathbf{r}_1')\psi(\mathbf{r}_1) | \Psi_n^N \rangle, & \omega_n > 0 \\ -e^{-i\omega_n t'}\langle \Psi_n^N | \psi^\dagger(\mathbf{r}_1')\psi(\mathbf{r}_1) | \Psi_0^N \rangle, & \omega_n < 0 \end{cases}$$
$$= -e^{-i\omega_n t'} X_n(\mathbf{r}_1', \mathbf{r}_1). \tag{111}$$

Thus Eq. (110) is now

$$X_n(\mathbf{r}_1', \mathbf{r}_1)e^{-i\omega_n t'} = -i\int d\mathbf{r}_2\,d\mathbf{r}_2'\,dt^2\{G_1(\mathbf{r}_1 t', \mathbf{r}_2 t^2)G_1(\mathbf{r}_2 t^2, \mathbf{r}_1' t')$$
$$\times V(|\mathbf{r}_2 - \mathbf{r}_2'|)X_n(\mathbf{r}_2', \mathbf{r}_2')$$
$$- G_1(\mathbf{r}_1 t', \mathbf{r}_2' t^2)G_1(\mathbf{r}_2' t^2, \mathbf{r}_1' t')V(|\mathbf{r}_2 - \mathbf{r}_2'|)$$
$$\times X_n(\mathbf{r}_2', \mathbf{r}_2)\}e^{-i\omega_n t^2}, \tag{112}$$

Multiplying both sides of (112) by $e^{i\omega_n t'}$; replacing the four G_1's by their Fourier integral representations, and integrating over t^2 to give δ-functions, which are then in turn integrated over, gives

$$X_n(\mathbf{r}_1', \mathbf{r}_1) = \frac{i}{2\pi}\int d\mathbf{r}_2\,d\mathbf{r}_2'\int d\varepsilon\{G(\mathbf{r}_1, \mathbf{r}_2; \varepsilon)G(\mathbf{r}_2', \mathbf{r}_1', \varepsilon - \omega_n)$$
$$\times V(|\mathbf{r}_2 - \mathbf{r}_2'|)X_n(\mathbf{r}_2', \mathbf{r}_2) - G(\mathbf{r}_1, \mathbf{r}_2, \varepsilon)G(\mathbf{r}_2, \mathbf{r}_1', \varepsilon - \omega_n)$$
$$\times V(|\mathbf{r}_2 - \mathbf{r}_2'|)X_n(\mathbf{r}_2', \mathbf{r}_2')\}. \tag{113}$$

In Appendix B the integrals over ε are carried out. If these results are used the definitions made that

$$V_{kl}(\mathbf{r}_3) = \int d\mathbf{r}_2\, f_k^*(\mathbf{r}_2)V(|\mathbf{r}_2 - \mathbf{r}_3|)g_l(\mathbf{r}_2)$$
$$\varphi_q = f_n, \qquad N_q = 0; \qquad \mathrm{Re}\,\varepsilon_q > 0 \tag{114}$$
$$\varphi_q = g_n, \qquad N_q = 1; \qquad \mathrm{Re}\,\varepsilon_q < 0,$$

the resulting equation is

$$X_n(\mathbf{r}_1', \mathbf{r}_1) = -\sum_{qq'}\frac{(N_{q'} - N_q)\varphi_q(\mathbf{r}_1)\varphi_q^*(\mathbf{r}_1')}{\varepsilon_q - \varepsilon_{q'} - \omega_n}$$
$$\times \int d\mathbf{r}_4\, V_{qq'}(\mathbf{r}_4)X_n(\mathbf{r}_4, \mathbf{r}_4)$$
$$+ \sum_{qq'}\frac{(N_{q'} - N_q)\varphi_q(\mathbf{r}_1)\varphi_q^*(\mathbf{r}_1')}{\varepsilon_q - \varepsilon_{q'} - \omega_n}$$
$$\times \int d\mathbf{r}_3\,d\mathbf{r}_4\,\varphi_q^*(\mathbf{r}_3)V(|\mathbf{r}_3 - \mathbf{r}_4|)\varphi_{q'}(\mathbf{r}_4)X_n(\mathbf{r}_4, \mathbf{r}_3). \tag{115}$$

The $(N_q - N_{q'})$ factor assures that only hole-particle X's are solved for (Schneider *et al.*, 1970).

A closed set of equations has finally been achieved. Equation (115) can be solved by standard non-Hermitian matrix diagonalization techniques. If the Dyson orbitals and energies are known the knowledge of the $X_n(\mathbf{r}_1, \mathbf{r}_2)$ and ω_n values enables the complete construction of only a special case of the general $R(121'2')$; namely, from (40d) the hole particle-$R^{\mathrm{hp}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2'; 0^+, 0^+)$; i.e.,

$$R(121'^{+}2'^{+}) = R^{\mathrm{hp}}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_1'\mathbf{r}_2'; 0^+0^+\varepsilon)$$
$$= \frac{1}{i}\sum_{\omega_n \neq 0}\frac{X_n(\mathbf{r}_1', \mathbf{r}_1)\tilde{X}_n(\mathbf{r}_2, \mathbf{r}_2')\,\mathrm{sgn}\,(\omega_n)}{\varepsilon - \omega_n + i\eta\,\mathrm{sgn}\,(\omega_n)}. \tag{116}$$

This and G_1 are all that is needed to calculate Σ in this approximation consistent with (107). This result is then substituted into Eq. (71), which result is in turn substituted into (67) to give [recall $U(2, 2^+) \equiv U(2)$]

$$\Sigma(1, 1') = \Sigma_{HF}(1, 1') - \int d2\, d3 V(1-2)G(1, 3)V(1'-3)R(321'^+2^+) + G(1, 1')\int d2\, d3 V(1-2)V(1'-3)R(32\,3^+2^+). \quad (117)$$

Noting the $\delta(t_1' - t_3)$ in $V(1'-3)$ indicates that the part of the general R needed in (117) is $R(t_1 t_2 t_1^+ t_2^+) = R(0^+, 0^+, t^1 - t^2)$ which is the Fourier transform of (116). In Fourier space equation (116) is

$$\Sigma_A(\mathbf{r}_1, \mathbf{r}_1', z) = \Sigma_{HF}(\mathbf{r}_1, \mathbf{r}_1') - \frac{i}{2\pi}\int d\mathbf{r}_2\, d\mathbf{r}_3\, dz' V(\mathbf{r}_1 - \mathbf{r}_2) \times R^{hp}(\mathbf{r}_3\mathbf{r}_2\mathbf{r}_3\mathbf{r}_2, 0^+0^+z')V(\mathbf{r}_3 - \mathbf{r}_1')G(\mathbf{r}_1, \mathbf{r}_1', z - z') + \frac{i}{2\pi}\int d\mathbf{r}_2\, d\mathbf{r}_3\, dz' V(\mathbf{r}_1 - \mathbf{r}_2)R_A(\mathbf{r}_3\mathbf{r}_2\mathbf{r}_1'\mathbf{r}_2, 0^+0^+z') \times V(\mathbf{r}_3 - \mathbf{r}_1')G(\mathbf{r}_1, \mathbf{r}_3, z - z'). \quad (118)$$

The final set of self-consistent approximate equations are, then, (1) Eq. (51) —the Dyson equation; (2) Eq. (115)—called the generalized R.P.A. equation; and (3) the formula in Eq. (118) after (115) is substituted in. The method of solution is then to start in Eq. (51) with $\Sigma_A \approx \Sigma_{HF}$ and solve for the Hartree–Fock orbitals and energies which are the φ_n and ε_n.

These are then introduced into (115) which now becomes the R.P.A. equation (since the φ's are φ_{HF}'s). The X's and ω_n's are found and combined with the φ_n's and ε_n's to form a new Σ. The procedure is repeated until self-consistency is achieved. On higher iterates Eq. (115) is no longer the R.P.A. equation but the G.R.P.A. equation. Equation (115) need be solved only for $\omega_n > 0$ as seen from (111). Once convergence is reached and G is known, Eq. (19) gives E_0, and Eq. (23) gives the one-particle density from which one-particle averages and natural orbitals can be found. As previously noted the ω_n are the excitation energies and the X_n give the generalized oscillator strengths. Of course R^{hp} is [compare Eqs. (64) and 116] the linear response (not the general response) from a generalization of the R.P.A. or coupled time-dependent Hartree–Fock (which are just different names for the same equation) which is consistent with the one-particle orbital equation.

The converged Σ_A can be put in (51) with $\varepsilon = q^2/2$ set to the desired scattering energy to give an equation for the $f_q^{(\pm)}$ of Eq. (76). These scattering orbitals, with the boundary conditions given in Eq. (79), can be solved for by any, and all, methods used for solving potential scattering problems (Reinhardt and Szabo, 1970). When solving for $f_q^{(\pm)}$ the finite basis set used in solving Equations (51) and (115) is no longer used. Equation (80b) with Σ_A substituted for Σ gives the approximate T matrix for elastic scattering. An approximate expression for inelastic scattering is obtained by substituting Eq. (108) into Eq. (83) which after Fourier transforming gives

$$S_{np,\,0q} = -\delta(\varepsilon_p - \varepsilon_q - \omega_n)\int d\mathbf{r}_1\, d\mathbf{r}_2\, V(\mathbf{r}_1 - \mathbf{r}_2) \times 2\pi\{f_p^{(-)*}(\mathbf{r}_1)f_q^{(+)}(\mathbf{r}_1)X_n(\mathbf{r}_2, \mathbf{r}_2) - f_p^{(-)*}(\mathbf{r}_1)f_q^{(+)}(\mathbf{r}_2)X_n(\mathbf{r}_2, \mathbf{r}_1)\}. \quad (119)$$

The approximate equation for inelastic scattering (119) is expected to be less accurate than the other approximate equations given in this section. The reason for this is that the truncation approximation (107) is closer in the hierarchy to the desired quantity than in the case of quantities depending on G_1. The philosophy of this approximation scheme is that a first-order approximation to Ξ when integrated over gives a moderately good R (or X_n), which when integrated over gives a good G_1. In the case of inelastic scattering, however, one is not integrating over R (thus averaging out its deficiencies), but using the X_n directly (and hence exposing them in their nakedness), so it would not be as surprising to see the approximation show deficiencies. If that proves to be the case, it will be necessary to either use higher order self-consistent sets of coupled equations (e.g., $\delta^2\Sigma \approx \delta^2\Sigma_{HF}$) or use higher order truncations of the Bethe–Salpeter equation as discussed in Section VI.

Clearly a generalization of Hartree–Fock theory has been achieved, with the advantage of overall self-consistency. The result is to give a theory that calculates with one basic approximation E_0, $\rho(1', 1)$, $S_{ok,\,ok'}$, $S_{op,\,nq}$, X_n, ω_n, and the linear response. Hopefully, if the scheme is performed on a finite basis set, the calculations will be tractable. In solving these equations, the non-Hermitian matrix diagonalization, the energy dependence of Σ, and the linear dependence of the set of Dyson orbitals, are all new but hopefully tractable problems.[19] The discrete basis set should not be any restriction since the φ's and R^{hp} represent phenomena that are localized in a small region of space.

[19] The linear dependance of the φ's means that the set is overcomplete hence new roots of Eq. (116) *may* show up at $\omega_n = 0$. Physically it is felt that these should be ignored and it is pleasing that the equation for R^{hp} has $\omega_n = 0$ omitted from the summation. The word "may" is stressed since in Eq. (116) X is seen to be expanded in the product space $\varphi_p \times \varphi_h$. So while the set φ_p, φ_h is overcomplete, and of course the product of two overcomplete sets in the product space, the partial, hole-particle, product is not necessarily overcomplete in the product space. In any case, such new roots, if they occur, will not cause any difficulty.

The successful computation, using such bases, of orbitals and frequency dependent moments for atoms and molecules is well documented.

The topic of the use of a discrete basis also brings up a point of caution. Equation (116) comes from Eq. (73) and is valid for bound-type functions only, i.e., functions that go to zero as $\mathbf{r}_1$ or $\mathbf{r}_2$ go to infinity. In a finite basis this is true of all functions obtained. If a method of solution is used which includes continuum functions, the continuum hole-particle amplitude equation, (89), will have to be used for the continuum amplitudes. After Eq. (107) is substituted in and the usual Fourier transform (the changes are essentially the same as for the bound state problem) taken, an equation is derived that is exactly as Eq. (116) except that $n \to \mathbf{p}_1$ m and an inhomogeneous term appears on the right-hand side which is simply the product of $\begin{Bmatrix}\text{outgoing}\\ \text{incoming}\\ \text{standing}\end{Bmatrix}$ wave particle and hole Dyson states with particle index $\mathbf{p}_1$ and hole index m, respectively. For the purpose of calculating R, the normalization of the Dyson orbitals does not matter since they differ by a phase factor which in turn causes the X's to have different phase factors which cancels in the product $X\tilde{X}$ appearing in (117).

A convenient matrix form of X is easily derivable even though the φ's are linearly dependent. Simply noting that Eq. (116) can be written as

$$X_n(\mathbf{r}_1', \mathbf{r}_1) = \sum_{\mathbf{q}\mathbf{q}'} \varphi_{\mathbf{q}}(\mathbf{r}_1)\varphi_{\mathbf{q}'}^*(\mathbf{r}_1')X_{\mathbf{q}\mathbf{q}'}^n \tag{120}$$

with

$$X_{\mathbf{q}\mathbf{q}'}^n = \frac{(N_{\mathbf{q}} - N_{\mathbf{q}'})}{\varepsilon_{\mathbf{q}} - \varepsilon_{\mathbf{q}'} - \omega_n}\left\{\int d\mathbf{r} V_{\mathbf{q}\mathbf{q}'}(\mathbf{r})X_n(\mathbf{r}, \mathbf{r}) - \int d\mathbf{r}\, d\mathbf{r}' \varphi_{\mathbf{q}}^*(\mathbf{r})V(|\mathbf{r} - \mathbf{r}'|)\varphi_{\mathbf{q}'}(\mathbf{r})X_n(\mathbf{r}', \mathbf{r})\right\}. \tag{121}$$

Substituting Eq. (120) into (121) gives the desired matrix form

$$(\varepsilon_{\mathbf{q}} - \varepsilon_{\mathbf{q}'} - \omega_n)X_{\mathbf{q}'\mathbf{q}}^n = (N_{\mathbf{q}} - N_{\mathbf{q}'})\sum_{\mathbf{p}\mathbf{p}'}[\langle \mathbf{q}\mathbf{p}'|V|\mathbf{q}'\mathbf{p}\rangle - \langle \mathbf{q}\mathbf{p}'|V|\mathbf{p}\mathbf{q}'\rangle]X_{\mathbf{p}'\mathbf{p}}^n \tag{122a}$$

where

$$\langle \mathbf{a}\mathbf{b}|V|\mathbf{c}\mathbf{d}\rangle = \int d\mathbf{r}\, d\mathbf{r}' \varphi_{\mathbf{a}}^*(\mathbf{r})\varphi_{\mathbf{b}}^*(\mathbf{r}')V(\mathbf{r} - \mathbf{r}')\varphi_{\mathbf{c}}(\mathbf{r})\varphi_{\mathbf{d}}(\mathbf{r}') \tag{122b}$$

Similarly the matrix form of R^{hp} is

$$R^{\mathrm{hp}}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_1'\mathbf{r}_2', 0^+0^+z) = \sum_{\substack{\mathbf{q}\mathbf{q}'\\ \mathbf{p}\mathbf{p}'}} \varphi_{\mathbf{q}}(\mathbf{r}_1)\varphi_{\mathbf{q}'}^*(\mathbf{r}_1')\varphi_{\mathbf{p}}(\mathbf{r}_2')\varphi_{\mathbf{p}'}^*(\mathbf{r}_2) \times R^{\mathrm{hp}}(0^+0^+z)_{\mathbf{q}'\mathbf{p}}^{\mathbf{q}\mathbf{p}'} \tag{123a}$$

with

$$R^{\mathrm{hp}}(0^+0^+z)_{\mathbf{q}'\mathbf{p}}^{\mathbf{q}\mathbf{p}'} = i\sum_{\omega_n \neq 0} \frac{X_{\mathbf{q}'\mathbf{q}}^n \tilde{X}_{\mathbf{p}'\mathbf{p}}^n}{\omega_n - z - i\varepsilon\,\mathrm{sgn}(\omega_n)}. \tag{123b}$$

Now that the basic approximate equations are exposed, a further discussion of the physics of the approximation is in order. Up to now the approximation has been introduced by appealing to the attractiveness of having higher order self-consistent theories which generalize the Hartree–Fock and the coupled time-dependent Hartree–Fock approximations. Also the point has been stressed that even if $\Sigma \approx \Sigma_{\mathrm{HF}}$ is not a very good approximation, $\delta\Sigma \approx \delta\Sigma_{\mathrm{HF}}$ may be a much less damaging one. Further justification for expecting that the approximation will give good results comes from the experience that the coupled time-dependent Hartree–Fock equation gives in actual calculation good frequency dependent responses (Dalgarno *et al.*, 1966), that the R.P.A. gives reasonable excitation energies (Dunning and McKoy, 1967) and that schemes which (i) use the R.P.A., (ii) solve for the ground state R.P.A. wave function, (iii) use the latter in place of $|\phi_o\rangle$ in (97) to solve for new orbitals, and (iv) use the orbitals in Eq. (115) to get new ω_n and X_n get generally improved agreement with experiment (Rowe, 1968; Gutfreund and Little, 1969) with only one iteration. Moreover, it has been shown that the types of correlation effects required in R, i.e., hole-particle effects (Kelly, 1968; Karplus and Caves, 1969) are all included in our iterated R. Note that the final linear response here is "nonlinear" in the sense that the zeroth order model has been greatly refined upon iteration.

Perhaps the most persuasive argument for the approximation comes from the physical model of elastic scattering that is implied. Here one starts with the Hartree–Fock virtual continuum orbital as the scattering orbital. This is called the static exchange approximation. The target electrons are also taken as in Hartree–Fock orbitals with Hartree–Fock exclusion correlations. The scattered or "test electron" in the virtual orbital now causes the target to respond, this response is calculated in the coupled time dependent Hartree–Fock (or R.P.A.) approximation. The response, which in this approximation is much better than perturbation theory applied to the Hartree–Fock Hamiltonian and which contains correlation and exchange effects and depends on the energy and position of the test particle, is then coupled with the Hartree–Fock orbitals (118) which "drive" the response to give a new effective potential. This potential is then used to calculate new target and scattering

orbitals. Everything is then iterated until the scattering orbital, the target orbital, and the response are all self-consistent. Since the electrons are all indistinguishable, the correlations in the target are as well represented as the ones between the test particle and the target; this must be reasonably well done since as said above, even the R.P.A. gives good responses.

To obtain the generalized R.P.A. equation for an electron scattering from an ion, in terms of quantities calculated for the neutral particle, (108) is substituted into (95) which after integrating over the delta functions gives

$$T^{\text{G.R.P.A.}}_{\mathbf{q}_1 m_1;\,\mathbf{q}_2 m_2} = i\int d1\; d2 f^{*(+)}_{\mathbf{q}_1}(1) g^{*}_{m_1}(2) V(1-2) X^{(+)}_{\mathbf{q}_2 m_2}(1, 2^+)$$

$$- i\int d1\; d2 f^{*(+)}_{\mathbf{q}_1}(1) g^{*}_{m_1}(1) V(1-2) X^{(+)}_{\mathbf{q}_2 m_2}(2, 2^+). \quad (124)$$

This can further be approximated by its first iterate the RPA. Then Σ is replaced by Σ_{HF} in the generalized R.P.A. equation (115), $f_{\mathbf{k}}{}^{+}(1)$ by $\varphi_{\mathbf{k}}{}^{+}(1)_{\text{HF}}$ and $g_m(2)$ by $\varphi_m(2)_{\text{HF}}$. These substitutions reduce Eq. (124) to

$$T^{\text{R.P.A.}}_{\mathbf{q}_1 m_1;\mathbf{q}_2 m_2} = i\int d1\; d2 \varphi^{*(+)}_{\mathbf{q}_1}(1)_{\text{HF}}\, \varphi^{*}_{m_1}(2)_{\text{HF}}\, V(1-2) X^{(+)}_{\mathbf{q}_2 m_2}(12^+)_{\text{R.P.A.}}$$

$$- i\int d1\; d2 \varphi^{*(+)}_{\mathbf{q}_1}(1)_{\text{HF}}\, \varphi^{*}_{m_1}(2)_{\text{HF}}\, V(1-2) X^{(+)}_{\mathbf{q}_2 m_2}(22^+)_{\text{R.P.A.}}. \quad (125)$$

where the X's are the first iterate to Eq. (115). Also making the above substitution in (105) reduces the $\bar{S}$ and $\tilde{S}$ matrices to their δ-function terms only. For the elastic R.P.A. case they become the unit matrix and the summations over $\mathbf{p}'$ and m' drop out. For the inelastic case the first term in (105) vanishes and in the second term there is only one nonzero term in the summation. We now remind the reader that the inelastic cross-section formula refer only to states that can be achieved by adiabatic coupling from a particle-hole independent particle state. For helium, there is only *one* particle-hole state, i.e., the $1s\mathbf{q}$ state and therefore for electron-helium scattering this formalism is not able to describe inelastic process at all. In Be one can think of two hole-particle states, i.e., $(1s)^2 2s\mathbf{q}$ and $(1s)(2s)^2\mathbf{q}'$; as such one can study elastic scattering on either of these states or inelastic scattering between them (though this inelastic process is not very interesting physically). We note also that even in the case where the formula can be applied for an inelastic process, the approximation is probably poor, because the R.P.A. is a refinement of the HF and the HF is not able to describe inelastic processes. The formula so obtained is well known as the R.P.A. elastic scattering formula (Dietrich and Hara, 1968; Lemmer and Veneroni, 1968). Dalgarno and Victor (1966) and Jamieson (1967) have used this equation by solving for X_n using the R.P.A. equation for X with G taken as G_{HF}, and with Hartree–Fock hole-particle

boundary conditions. They solved this R.P.A. scattering elastic formula for the p-wave phase shift for the elastic scattering of an electron off a helium positive ion. Their agreement with the close coupled results of Burke and McVicar (1965) was quite good. Although obvious, it should be mentioned that in molecular systems, noting the facts that (1) for each geometry, excitation energies are calculated self-consistently and directly, and (2) Eq. (19) can be used to get the consistent absolute energy of the ground state (hopefully the errors in this formula will not be very sensitive to the geometry changes), implies that all potential surfaces of the molecule can be calculated self-consistently in one calculation.

VI. Perturbation Methods[20]

A. G^0 Perturbation Method

One of the most straightforward ways (in principle) of solving for the one-particle Green's function is as a perturbation expansion in terms of a "bare" or "free particle" (or unperturbed) Green's function G^0 and the residual interaction potential V. G^0 satisfies the equation of motion (47a) where $h(1)$ is some suitable single particle Hamiltonian (e.g., free particle, Hartree, or Hartree–Fock) leaving over an interaction potential $V(1-2)$. While there are many ways to develop a perturbation series, we shall use the Dyson equation (48‴) and substitute the self-energy expressed in terms of the functional derivative of G, obtained from substituting (56b) into (47b'),

$$\Sigma(1,1') = -i\delta(1-1')\int d2 V(1-2) G(2, 2^+)$$

$$+ i\int d2\; d2' V(1-2)\frac{\delta G(1,2')}{\delta U(2)} G^{-1}(2', 1') \quad (126)$$

yielding

$$G(1,1') = G^0(1,1') - i\int d2\; d2' G^0(1,2) V(2-2')$$

$$\times\left[G^0(2', 2'^+) - \frac{\delta}{\delta U(2')}\right] G(2, 1'). \quad (127)$$

To develop a perturbation expansion, one just iterates on Eq. (127), that is, one first substitutes $G^0(2, 1')$ for $G(2, 1')$ on the right-hand side and evaluates the resulting expression

[20] See Matsubara (1955), Martin and Schwinger (1959), Falkoff (1962), Roman (1965), March *et al.* (1967), Kirzhnits (1967), Mattuck (1967).

$$G(1,1') = G^0(1,1') - i\int d2\,d2' G^0(1,2)V(2-2')$$

$$\times\left[G^0(2',2'^+) - \frac{\delta}{\delta U(2)}\right]G^0(2,1') + \text{higher order terms}, \quad (128)$$

obtaining the lowest order corrections to G^0. If one wishes to go further, one substitutes the lowest order terms back into (127) and repeats the process.

Clearly in order to solve Eq. (128) we must be able to evaluate terms such as

$$[\delta/\delta U(2)]G^0(1,1').$$

Varying

$$\int d2[G^0(1,2)]^{-1}G^0(2,1') = \delta(1-1')$$

yields

$$\frac{\delta G^0(1,1')}{\delta U(2)} = -\int d3\,d3' G^0(1,3)\frac{[\delta G^0(3,3')]^{-1}}{\delta U(2)}G^0(3',1')$$

where $[G^0]^{-1}$ satisfies [in the presence of the external potential $U(2)$]

$$[G^0(1,1')]^{-1} = [i(\partial/\partial t_1) - h(1) - U(1)]\delta(1-1')$$

hence

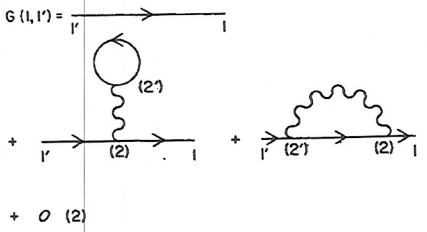
$$\frac{\delta G^0(1,1')}{\delta U(2)} = G^0(1,2)G^0(2,1'). \quad (129)$$

This equation is the basic result necessary to develop a perturbation expansion. One should note that the right-hand side of Eq. (129) is an ordinary product and not an operator product. Substituting (129) into (128) yields the Green's function correct to first order in the interaction potential

$$G(1,1') = G^0(1,1') - i\int d2\,d2' G^0(1,2)V(2-2')$$

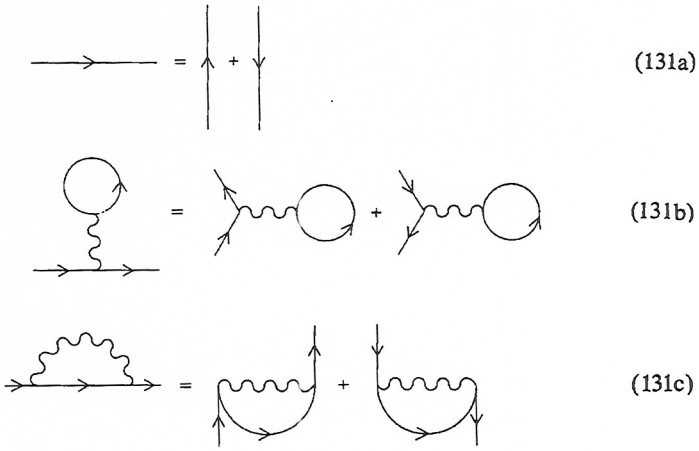
$$\times[G^0(2',2'^+)G^0(2,1') - G^0(2,2')G^0(2',1')] + O(2). \quad (130)$$

It is useful at this point to look at a diagrammatic interpretation of Eq. (130).



(130′)

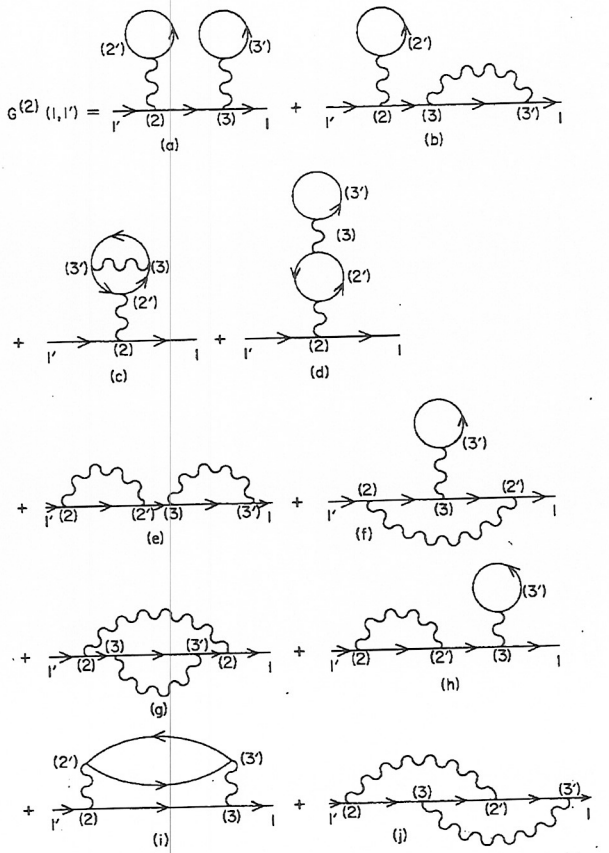
In (130′) the diagrams correspond one to one with the three terms on the right-hand side of Eq. (130). However, note that there is, as yet, no indication of the signs of the terms (we shall discuss how to determine the sign of a diagram presently). To interpret the diagrams one reads a straight line as a G^0 with the space time points at the two ends of the line as its arguments. A wavy line is a V interaction between the space time points at its two ends (remember that V has a δ-function of its time arguments denoting an instantaneous interaction). All internal points in parentheses are to be integrated over. Recall that since in the Green's function both time orderings are present they represent both particle and hole propagators and all time orderings consistent with instantaneous interactions are implied. One can easily go over to the more common Goldstone diagrams (Goldstone, 1957) by taking account of the above orderings



Hence (131a) depicts the propagation of a "free" particle or "free" hole depending on the time ordering; (131b) is the interaction of a particle (hole) with a passive particle, and (131c) is the exchange term of (131b). Clearly these diagrams describe the Hartree–Fock interaction. By looking at Eq. (130) we see that (131b) and (131c) are multiplied by (i) and (131b) comes in with a negative sign. The general rule is to multiply each diagram by $(i)^n$, where n is the number of V interactions (wavy lines, i.e., the order of perturbation theory) in the diagram and also multiply each diagram by $(-1)^l$ where l is the number of closed loops composed solely of G^0 lines [notice (131b) has $l=1$, (131c) has $l=0$].

To proceed to second order one merely replaces the G on the right-hand

side of the Dyson equation (127) by the first-order G, Eq. (130), and again uses (129) to evaluate the functional derivatives. Rather than write out the analytic forms for the second-order corrections to G we shall draw the diagrams



(132)

As an example of going from the diagram to the analytic form of a perturbation term we shall write the formula for term (i). Reading from right to left on the diagram there is a $G^0(1, 3)$; a $V(3—3')$; three G^0 lines: $G^0(3, 2)$; $G^0(3', 2')$, and $G^0(2', 3')$; then there is a $V(2' - 2)$; followed by a $G^0(2, 1')$. The integration is over space time points 2, 2', 3, and 3'. Since there are two V lines there is a factor $(i)^2$, and one closed loop there is a factor (-1). Thus,

$$(132\text{i}) = (-i)^2 \int d2\, d2'\, d3\, d3' G^0(1, 3) V(3 - 3') G^0(3, 2)$$
$$\times G^0(3', 2') G^0(2', 3') V(2 - 2') G^0(2, 1').$$

The only point not illustrated in the above example is when a G^0 line begins and ends on the same vertex, such as in (132h), this is written as $G^0(3', 3'^+)$.

Thus the rules for obtaining a perturbation expansion of G in terms of G^0 and V can be summarized as follows:

(1) G is the sum of all topologically distinct connected diagrams through the desired order in the interaction with two external solid lines. (Diagrams which differ only in their time ordering are not distinct, e.g., interchanging $(2) \leftrightarrow (3)$ and $(2') \leftrightarrow (3')$ in (131e) does not lead to a different diagram.) A diagram is connected if every vertex is connected to at least one other vertex by at least one G^0 or V line (i.e., it is not composed of disconnected pieces).

(2) Interpret each straight line as a G_0 function of its end points reading from right to left. If there is any ambiguity in time interpret the furthest right point as having a + on it.

(3) Interpret the wavy lines as V functions of its end points.

(4) Integrate over the space time arguments of all internal points.

(5) Give each diagram a multiplicative factor of $(i)^n$, where n is the number of V lines.

(6) Give each diagram a multiplicative factor of $(-1)^l$, where l is the number of closed loops made up solely of G_0 lines.

In order to transform the perturbation series to a sum over states one first goes over to an energy dependent representation by introducing the time Fourier transformed G^0's in their spectral expansion form, Eq. (53b). One then integrates over the ε's instead of the times taking care to include the δ-functions coming from the V's and the infinitesimal positive and negative imaginary contributions to the energy denominators coming from the particle and hole terms, respectively.

The major difficulties with the G^0 perturbation method are concerned with rapidity of convergence. This becomes most evident from the fact that while G has poles off the real axis (on the nonphysical sheets) G^0 does not. Hence, one is building up the damping terms in G by a series expansion which does not converge rapidly for large times.

B. Σ Perturbation Method

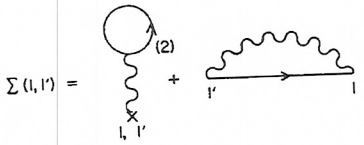
If we know the self-energy operator, then we can solve the non-Hermitian eigenvalue equation for G as described in Section III. Hence as an alternative to obtaining G directly in a perturbation series one can develop a perturbation series for Σ and then solve for G. This can be done by resumming the G

perturbation series, or by again using the technique of functional differentiation. The procedure is much the same as that used in the preceding section.

Starting with Eq. (61) for Σ as a function of V, G, and $\delta\Sigma/\delta U$ the lowest order terms in Σ are obtained by just replacing the G's in the first two terms on the right-hand side of (61) by G^0's yielding

$$\Sigma(1,1') = -i\delta(1-1')\int d2V(1-2)G^0(2,2^+) + iV(1-1')G^0(1,1') + O(2) \tag{133}$$

or diagrammatically



+ O (2). (133′)

Clearly, this procedure can be continued by putting higher order terms in the perturbation expansion for G into the first two terms on the right-hand side of Eq. (61). There are also terms in the expansion for Σ which come from the third term on the right-hand side of (61). We shall evaluate the lowest order terms (second) coming from this third term by substituting G_0 for G and (133) for Σ, yielding

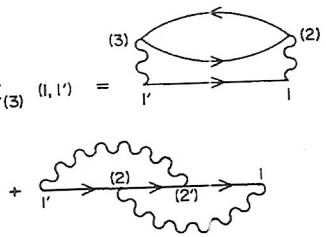
$$i\int d2\,d2'V(1-2)G(1,2')\frac{\delta\Sigma(2',1')}{\delta U(2)} = \Sigma_{(3)}(1,1')$$

$$= i\int d2\,d2'V(1-2)G^0(1,2')\frac{\delta}{\delta U(2)} \times\left[-i\delta(2'-1')\int d3V(2'-3)G^0(3,3') + iV(2'-1')G^0(2',1')\right] + O(3).$$

Using Eq. (129) for $\delta G^0/\delta U$ and integrating the first term over $2'$

$$\Sigma_{(3)}(1,1') = -(i)^2\int d2\,d3V(1-2)G^0(1,1')V(1'-3)G^0(3,2)G^0(2,3^+) + i^2\int d2\,d2'V(1-2)G^0(1,2')V(2'-1')G^0(2',2)G^0(2,1') + O(3) \tag{134}$$

or diagrammatically



+ O (3). (134′)

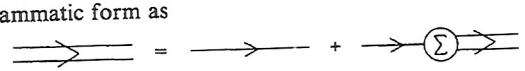
One should notice that all of the diagrammatic rules given in Section VI,A for the perturbation expansion of G carry over unchanged for the perturbation expansion of Σ except for rule (1) which is modified as follows:

(1′) Σ is the sum of all topologically distinct *strongly* connected diagrams through the desired order in the interaction with no external lines (however, there are two vertices which are not to be integrated over and have the space time designations of the two arguments of Σ). A connected diagram is strongly connected if it does not fall into two disconnected pieces when any single straight line, i.e., Green's function line, is cut. For example, 132c,d,f,g,i,j are strongly connected second-order diagrams, the rest of (132) are not.

The reason for the changes in rule (1) can be easily seen by expressing the Dyson equation (48‴)

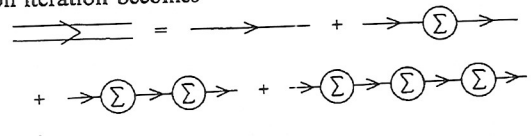
$$G = G^0 + G^0\Sigma G$$

in diagrammatic form as



(135)

which on iteration becomes



(136)

From (136) we see that all weakly connected diagrams in G are composed of strongly connected Σ pieces connected by a single G^0 line. Hence, if we had included weakly connected diagrams in Σ we would have overcounted them when the equation of motion is solved for the resulting G.

Hence, the Σ perturbation method is to solve for the self-energy perturbationally to the desired order and then to solve the equation of motion for the resulting Green's function. While one has to do more work than in the Green's function perturbation method, in that one must also solve the non-Hermitian eigenvalue problem, one gets considerably more out of the method.

It is equivalent to iterating the diagrams considered in Σ to all orders in G [see (136)]. Naturally this implies that a smaller number of perturbational terms must actually be solved for in order to obtain good answers. Of course one can never show in any partially summed method that one is not losing some cancellation with diagrams that are not being considered. However, one hopes that by considering the most important diagrams in Σ (perhaps one should consider this as a "model" self-interaction) and solving its equation of motion exactly will lead to useful results. Only future theoretical experimentation will tell.

It is important to realize that it is the ability to solve the equation of motion for the Green's function on a finite basis set for atoms and molecules that makes the Σ perturbation expansion a practical calculational method.

C. Renormalized Σ Perturbation Method

One can also develop a renormalized or self-consistent perturbation expansion for Σ in terms of the interaction V and the full Green's function G (not the "free particle" G^0). One can obtain the expansion analytically using much the same functional differentiation method as that employed in the previous two sections; however, it is so easy to see diagrammatically that we shall proceed in that fashion.

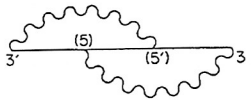
The diagrams in the renormalized perturbation expansion are again interpreted as in Section VI,A except that the straight lines will now denote the full one-particle Green's function, and rule (1) which gives the class of diagrams to be summed must again be modified as follows:

(1″) Σ is the sum of all topologically distinct strongly connected *basic* diagrams with the desired number of interaction lines, full Green's function lines, and no external lines (there are two free vertices). A diagram is a *basic* diagram if it cannot be constructed by inserting other diagrams into the Green's function lines. For example,

(137a)

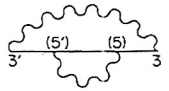
and

(137b)



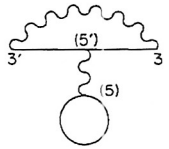
(137c)

are basic, but



(138a)

and



(138b)

are not. [Note that (137b and c) are the only second-order basic diagrams].

The reason for excluding insertion diagrams is that when the full Green's function line is expanded as in (136) all insertion diagrams are included in the G line. Hence, putting them into the class of renormalized Σ diagrams will overcount them.

Thus, there is a practical scheme for self-consistently solving for G using the renormalized Σ perturbation expansion:

(i) Take a set of strongly connected basic Σ diagrams, correct to the desired order, and solve for Σ interpreting the Green's function lines as "bare" G^0 lines.

(ii) Solve the equation of motion for the resulting G, which will be obtained in a spectral expansion form.

(iii) Repeat step (i) now using the result of step (ii) for the Green's functions.

(iv) Repeat step (ii) now using the result of step (iii) for Σ, and repeat until self-consistency is achieved.

Again we see that in the self-consistent perturbation method one must do more work, in the sense of repeatedly solving the same set of equations until self-consistency is achieved. However, again, one obtains more results for more work in that not only iterates of the basic diagrams considered in Σ are obtained to all orders in G, but one also obtains all diagrams which can be constructed by insertion of the basic diagrams into Green's function lines (to all orders) with these multiple insertion diagrams also iterated to all orders in G. Thus, we would expect that starting with a rather small number of basic Σ diagrams solved for perturbationally would give good answers in the

self-consistent perturbation method. Again, it is our ability to solve the equation of motion for G in a finite basis set which makes this self-consistent perturbation approach practical for atomic and molecular calculations.

D. Perturbation Methods for R and X_n

From the discussions in the previous sections it is evident that if one is interested in problems where there is a transition of the target system from one state to another, e.g., excitation energies, inelastic scattering, etc., then knowledge of G_1 is insufficient and one must look at the information contained in G_2 (or equivalently R). For this reason perturbation methods of solving for R, and X_n, will now be derived. The hierarchy of perturbation methods will be derived in the opposite order from that of the previous subsections. That is, first an expansion for Ξ in terms of G_1 will be derived to be used in conjunction with the Bethe–Salpeter equation to find R (or X_n) as a function of G_1, V, and R (or X_n) itself; this is analogous to the Σ perturbation method where Σ is used in conjunction with the Dyson equation to obtain G_1. Then by expanding the Bethe–Salpeter equation a perturbation expression for R directly in terms of G_1 and V is derived (thus eliminating the need to solve the Bethe–Salpeter integral equation if one so desires). That such perturbation expansions can be derived is, of course, obvious, since their derivation just undoes the work of Bethe and Salpeter in summing the perturbation series to obtain an integral equation in the first place. The present philosophy is that it is preferable to derive perturbation expansions by expanding closed equations derived analytically rather than to sum perturbation series to obtain closed expressions.

Since Ξ is defined as $\delta\Sigma/\delta G_1$ [Eq. (67)] a perturbation expansion for Ξ can be obtained by simply differentiating the expansion for Σ as a function of G_1, obtained in Section VI, C, with respect to G_1. Using the first-order correction to Σ, Equation (133) with the $G_1{}^0$'s replaced by G_1's (this is equivalent to functionally replacing Σ by the Hartree–Fock approximation to Σ) one obtains

$$\Xi^{(1)}(34\,3'4') = i\frac{\delta}{\delta G(4',4)}\Big\{-\delta(3-3')\int d5V(3-5)G(5,5^+) + V(3-3')G(3,3')\Big\}$$

$$= i\Big\{\delta(3-3')\int d5V(3-5)\frac{\delta G(5,5^+)}{\delta G(4',4)} + V(3-3')\frac{\delta G(3,3')}{\delta G(4',4)}\Big\}$$

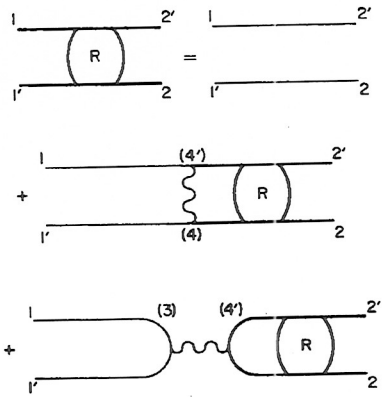
$$= -i\,\delta(3-3')\int d5V(3-5)\,\delta(5-4')\,\delta(5^+-4) + iV(3-3')\,\delta(3-4')\,\delta(3'-4)$$

$$= -i\delta(3-3')\,\delta(4-4')V(3-4') + iV(3-3')\,\delta(3-4')\,\delta(3'-4). \tag{139}$$

Equation (139) is now inserted into the Bethe–Salpeter equation (68) and integrated over the δ-functions to give

$$R(121'2') = G(1,2')G(2,1') + i\int d4\,d4'G(1,4')G(4,1')V(4-4') \times R(4'242') - i\int d3\,d4'G(1,3)G(3,1')V(3-4')R(4'24'^+2') + O(2) \tag{140}$$

which is the same equation obtained in Section V by using $\Sigma = \Sigma_{HF}$, Eq. (106). Equation (140) can be expressed diagrammatically as

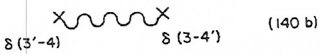


(140′)

where the heavy lines depict the R lines and the light lines are G_1 lines. The analytic expression corresponding to (140'a) carries a factor of (i) and that corresponding to (140'b) a factor of $(-i)$.

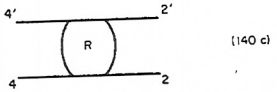
To obtain the second-order terms in Ξ one can just take the analytic expression for the second-order expression for Σ as a function of G_1, which is given by the basic diagrams (137b) and (137c) and perform the differentiation

as above. However, it is more convenient, and much simpler, to perform this completely diagrammatically. It is clear looking at the Σ diagram, (137a), which leads to (140′a) that taking the derivative with respect to $G(4', 4)$ just deletes the Green's function line $G(3, 3')$ and gives two δ-function factors $\delta(3 - 4')$ and $\delta(3' - 4)$



(140 b)

When this diagram is put into the Bethe–Salpeter equation and the δ-functions are integrated over the diagram is just linked up to the R diagram



(140 c)

with the δ-functions telling where the linkages go, the "free" vertices of the original Σ diagram (which in this case are also 3′ and 3) are linked up with the two Green's function lines $G(1, 3)$ and $G(3', 1')$, and the intermediate points are integrated over leading to (140′a). Also since the original diagram carried a factor of (i) (one V line, no closed loops) so does the analytic expression corresponding to this diagram. Thus, there are a set of rules similar to those of the previous subsections for constructing the Bethe–Salpeter diagrams for R as a function of V, G_1, and R itself to a given order in the interaction.

R is the sum of all topologically distinct Bethe–Salpeter diagrams constructed by

(1) Taking the basic strongly connected diagrams for Σ (in terms of G_1 and V) to the desired order.

(2) Erasing an internal G line in each of the Σ diagrams and connecting its exposed vertices to the free ends of the R diagram lines.

(3) The free vertices of the original Σ diagram are each connected up to a G line.

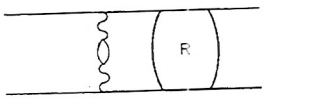
(4) Step (2) [followed by step (3)] is repeated for each topologically distinct internal G line in each of the considered Σ diagrams.

The analytic formula corresponding to a given diagram is obtained in the same way as in the previous subsections, remembering that the G lines are now full G lines, with the following two exceptions:

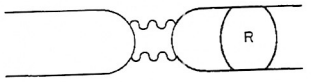
(i) The factor $(-1)^l$ must be obtained from the Σ diagram before erasing the G line since one can open up a closed loop by erasing a line.

(ii) If the G line being erased has g other topologically equivalent G lines the diagram carries a weight factor g, rather than repeating the diagram g times.

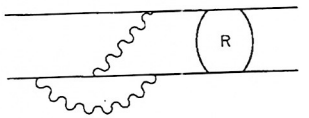
As an example of the use of these rules, we shall now obtain the Bethe–Salpeter diagrams for the second-order corrections to R. The two second-order basic diagrams are (137b) and (137c). Applying the above rules leads to the following four topologically distinct Bethe–Salpeter diagrams



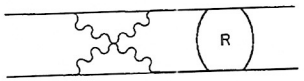
(141a)



(141b)



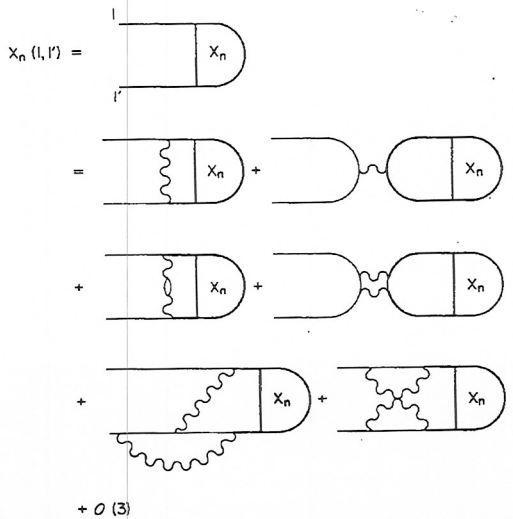
(141c)



(141d)

Diagram (141a) comes from (137b) by erasing the 3′—3G line. Diagram (141b) is obtained by erasing either of the two 5′—5 lines in (137b) and hence carries a weight factor of 2. Diagram (141c) is obtained from (137c) by erasing either of the two topologically equivalent G lines 3′—5 or 5′—3, hence it also carries a weight factor of 2. Diagram (141d) comes from erasing the 5—5′ G line in (137c). Diagrams (141a and b) have a factor of (-1) since (137b) has one closed loop, and all four have a factor of $(i)^2$ since there are two V lines.

Since the Bethe–Salpeter amplitude equation (73) for X_n is of exactly the same form as that for R (except that X_n has only two variables), one can immediately write down the perturbation expansion for X_n. All that is necessary is to define a symbol for X_n which has only two free lines corresponding to the two variables. Hence, X_n correct through second order is given by



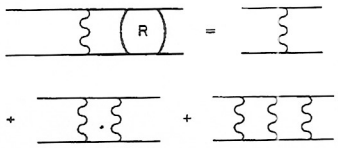
(142)

where the terms have exactly the same interpretation (except for replacing the R piece in each diagram by an X_n piece) as those in the Bethe–Salpeter expansion for R.

Clearly, a self-consistent scheme of solution for G_1 and R is possible. That is, the Bethe–Salpeter perturbation series is truncated at some point. Then assuming a G (usually the Hartree–Fock G) one solves the truncated Bethe–Salpeter integral equation for R (or the X_n's). Then knowing R one has the Σ for solving the Dyson equation for G, as was discussed in Section III. The Dyson equation is then solved for G keeping Σ fixed. This G is then inserted back into the truncated Bethe–Salpeter equation and the process is repeated until self-consistency between G_1 and R is obtained. The above procedure is obviously a higher order (and more difficult) procedure than the self-consistent procedure described in Section VI, C, since it requires the self-consistent solution of a coupled pair of integral equations, and the Bethe–Salpeter equation now has an energy dependent kernel. The self-consistent method described in Section V as the generalized R.P.A. method is the lowest order case of the method described above, that is, the Bethe–Salpeter perturbation expansion is truncated at first order (a simple superposition approximation for G_2 is the truncation of the expansion at zeroth order which obviously eliminates the Bethe–Salpeter integral equation). Clearly higher order truncations will work better (especially for transition problems where one really needs R, or X_n) and also be correspondingly more work.

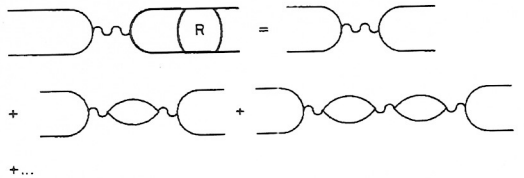
As an alternative to the above Bethe–Salpeter perturbation series (which is really a perturbation series for Ξ which is then inserted into the Bethe–

Salpeter integral equation) the truncated expansion can be iterated thus eliminating the integral equation in favor of its perturbation expansion. This step undoes the original summation derivation of the integral equation. Diagrammatically this is just done by iterating the diagrams. That is, first replace the R part of a diagram by the zeroth order result (two G lines) thus obtaining the lowest order approximation to the original diagram. This is then used to replace R in the original diagram obtaining a higher order approximation, etc. For example, iterating one of the first order Bethe–Salpeter diagrams (140'a) gives



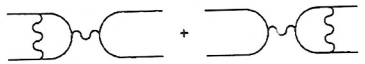
(143a)

which is the "ladder" diagram series. Similarly just iterating (140'b) gives the "bubble" diagram series.



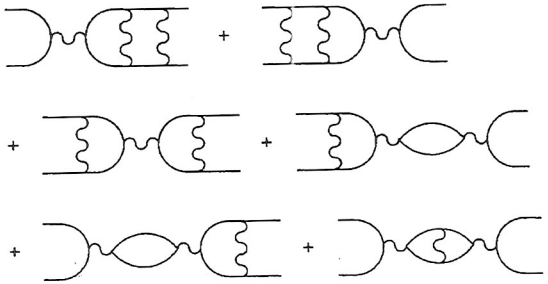
(143b)

There are also clearly combination diagrams of ladders and bubbles if one takes both (140'a) and (140'b) into account together by iterating all of (140'), such as



(143c)

to second order, and



to third order. The sum of all of the diagrams in (143) plus, of course, the diagram consisting of two G_1 lines gives the third-order perturbation approximation to the first order Bethe–Salpeter equation (140).

This iteration can clearly be performed to any desired order starting with any set of Bethe–Salpeter diagrams, thus obtaining a truncated expression for R in terms of V and G_1 only. For a given set of Bethe–Salpeter diagrams one can thus eliminate having to solve the integral equation to find R. A price is again paid for this simplification in the amount of work, since the integral equation sums the diagrams to all orders and here one only sums to a finite order.

Again, an iterative process can be carried through for self-consistently solving for R and G_1. It is, however, exactly equivalent to the renormalized Σ self-consistent method described in Section VI, C, since knowing R (as a function of G and V) to any given order is equivalent to knowing Σ (as a function of G and V) to that order.

Lower order approximations to R can be obtained by replacing the G_1 lines in diagrams like those of (143 a, b, c, d) by some perturbational approximation to G_1 as formulated in Section VI, A. R is then given by a perturbation expansion containing only $G_1{}^0$'s and V's. Now it is no longer possible to solve for R and G_1 self-consistently, since G_1 does not appear in the truncated expression for R. Of course, R can be used together with the Dyson equation to solve for G_1, but this is equivalent to the use of unrenormalized Σ perturbation theory as described in Section VI, B.

ACKNOWLEDGMENTS

The authors acknowledge the kind help and interest of Dr. Barry Schneider, who initiated the application of Green's functions in electron-atom scattering theory, and who has had numerous enlightening discussions with the present authors. They are also grateful to Mr. B.-S. Yarlagadda for several interesting remarks. The authors appreciate also the kindness of Mr. Lowell Thomas and Mr. Ju Chu Ho for reading and correcting the manuscript.

Appendix A

The Derivation of the Schwinger Relation

It is useful to write $G(1, 1'; U)$ in terms of the quantities appearing in the case when U is zero, which is accomplished by going over to the interaction representation. To do this, the homogeneity of time is used to set the time at which the Heisenberg representation (in terms of which Equation (54) is written) and the interaction representation are equivalent at time $t = -\infty$.

At this time $|\Psi_0(U)\rangle = |\Psi_0\rangle$. To go over to the interaction representation one uses a generalization of Eq. (2) for a time-dependent Hamiltonian

$$Op(i)_{\text{Heisenberg}} = T\exp\left[i\int_{-\infty}^{t} d\tau H(\tau)\right] Op(\mathrm{r}_i)_{\text{Schroedinger}} T\exp\left[-i\int_{-\infty}^{t} d\tau H(\tau)\right]$$

The time ordering is necessary (Dyson, 1949; Feynman, 1951) because the Hamiltonian taken at two different times does not in general commute, hence the power series expansion of the exponential would be ambiguous as to the ordering of the operator. The time-ordering operator defines the ordering and hence removes the ambiguity. Thus

$$\begin{aligned}
\psi_n(1) &= T\exp\left[i\int_{-\infty}^{t} d\tau H(\tau)\right]\psi(\mathrm{r})T\exp\left[-i\int_{-\infty}^{t} d\tau H(\tau)\right] \\
&= T\exp\left\{i\int_{-\infty}^{t} d\tau[H + H_{\text{int}}(\tau)]\right\}\psi(\mathrm{r})T\exp\left\{-i\int_{-\infty}^{t} d\tau[H + H_{\text{int}}(\tau)]\right\} \\
&= T\exp\left[i\int_{-\infty}^{t} d\tau H_{\text{int}}(\tau)\right]\exp\{iH[t-(-\infty)]\}\psi(\mathrm{r}) \\
&\quad \times \exp\{-iH[t-(-\infty)]\}T\exp\left[-i\int_{-\infty}^{t} d\tau H_{\text{int}}(\tau)\right] \\
&= T\exp\left[i\int_{-\infty}^{t} d\tau H_{\text{int}}(\tau)\right]\psi(1)\exp\left[-i\int_{-\infty}^{t} d\tau H_{\text{int}}(\tau)\right] \qquad \text{(A.1)}
\end{aligned}$$

where use was made of the fact that the time-ordered exponential of a sum is equal to the time-ordered product of exponentials (this, of course, is not true without time ordering for noncommuting operators) and where

$$\int d\tau\, H_{\text{int}}(\tau) = \int d2\, d2' U(2', 2)\psi^\dagger(2')\psi(2) \qquad \text{(A.2)}$$

which since the time ordering is specified as $t_2' > t_2$ can be written as

$$\int d\tau\, H_{\text{int}}(\tau) = -\int d2\, d2' U(2', 2) T[\psi(2)\psi^\dagger(2')]. \qquad \text{(A.3)}$$

Defining

$$S(t, t') = T\exp\left[-i\int_{t'}^{t} d\tau\, H_{\text{int}}(\tau)\right] \qquad \text{(A.4)}$$

Eq. (54) becomes

$$G(1, 1'; U) = \frac{1}{i}\langle\Psi_0|\, TS(-\infty, t)\psi(1)S(t, t')\psi^\dagger(1')S(t', -\infty)|\Psi_0\rangle. \qquad \text{(A.5)}$$

Using the fact that $U = 0$ at $t = +\infty$, $\Psi_0(U)$ is again Ψ_0 (to within an

unobservable infinite phase), the $\langle\Psi_0|$ at $t=-\infty$ can be replaced by the $\langle\Psi_0|$ at $t=+\infty$ using

$$\langle\Psi_0(-\infty)| = \frac{\langle\Psi_0(+\infty)|S(+\infty,-\infty)}{\langle\Psi_0(+\infty)|S(+\infty,-\infty)|\Psi_0(-\infty)\rangle} \tag{A.6}$$

where the denominator accounts for the phase and preserves normalization. Equation (A.6) is justified by a series of steps quite similar to that gone through in (A.1). Substituting (A.6) into (A.5), moving $S(+\infty,-\infty)$ to be thought of as $\lim_{\substack{t\to\infty\\ t'\to-\infty}} S(t,t')$ under the T (which can be done since $T^2=T$) and combining the exponentials in the S's gives

$$G(1,1';U) = \frac{1}{i}\frac{\langle\Psi_0|T[S(+\infty,-\infty)\psi(1)\psi^\dagger(1')]|\Psi_0\rangle}{\langle\Psi_0|S(+\infty,-\infty)|\Psi_0\rangle}. \tag{A.7}$$

This is the desired expression for $G_1(1,1';U)$ in terms of the quantities that appear in G_1 for $U=0$. To evaluate $\delta G_1(U)/\delta U$ in the limit of small U, let $U\to U+\delta U$ (where δU is an arbitrary infinitesimal change in U) and thus $H_{\text{int}}\to H_{\text{int}}+\delta H_{\text{int}}$ and $G\to G+\delta G$. The change in S arising from the infinitesimal change in U is given by

$$T\exp\left\{-i\int_{t'}^{t}d\tau[H_{\text{int}}(\tau)+\delta H_{\text{int}}(\tau)]\right\} - T\exp\left\{-i\int_{t'}^{t}d\tau[H_{\text{int}}(\tau)]\right\} = TS(t,t')\left\{-i\int_{t'}^{t}d\tau\delta H_{\text{int}}(\tau)\right\} \tag{A.8}$$

yielding

$$G(1,1';u)+\delta G(1,1';U) = -i\frac{\langle TS(+\infty,-\infty)[1-i\int_{-\infty}^{\infty}d\tau\delta H_{\text{int}}(\tau)]\psi(1)\psi^\dagger(1')\rangle}{\langle TS(+\infty,-\infty)[1-\int_{-\infty}^{\infty}d\tau\delta H_{\text{int}}(\tau)]\rangle}. \tag{A.9}$$

If the denominator is expanded in powers of δH_{int}, and only the lowest order term in the infinitesimal is retained then Eq. (A.9) gives, after (A.7) is used to subtract $G_1(U)$ from both sides

$$\delta G(1,1';U) = -i\left\{-i\left\langle TS(\infty,-\infty)\left[\int d\tau\,\delta H_{\text{int}}(\tau)\psi(1)\psi^\dagger(1')\right]\right\rangle - G(1,1';U)\langle TS(\infty,-\infty)\int d\tau\delta H_{\text{int}}(\tau)\rangle\right\}\times\langle S(\infty,-\infty)\rangle^{-1} \tag{A.10}$$

which after substituting (A.3) into (A.10) yields

$$\delta G(1,1';U) = \left\{\int d2\,d2'\langle TS(\infty,-\infty)\psi(2)\psi^\dagger(2')\psi(1)\psi^\dagger(1')\rangle \times\delta U(2',2)+\frac{1}{i}G(1,1';U)\int d2\,d2'\langle TS(\infty,-\infty)\psi(2)\psi^\dagger(2')\rangle \times\delta U(2',2)\right\}\times\langle S(\infty,-\infty)\rangle^{-1}. \tag{A.11}$$

Permuting the creation and annihilation operators under T, with proper sign changes to give the order of the definitions of G_1 and G_2 as given by Eq. (1) gives

$$\delta G(1,1';U) = \left\{-\left(\frac{1}{i}\right)^2\int d2\,d2'\langle TS(\infty,-\infty)\psi^\dagger(1')\psi(2) \times\psi^\dagger(2')\psi(1)\rangle\delta U(2',2)+\frac{1}{i}G(1,1';U)\int d2\,d2' \times\langle TS(\infty,-\infty)\psi(2)\psi^\dagger(2')\rangle\delta U(2',2)\right\}\langle S(\infty,-\infty)\rangle^{-1}. \tag{A.12}$$

The functional derivative is then

$$\frac{\delta G_1(1,1';U)}{\delta u(2',2)} = \left\{-\left(\frac{1}{i}\right)^2\langle TS(\infty,-\infty)\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')\rangle +\frac{1}{i}G(1,1';U)\langle TS(\infty,-\infty)\psi(2)\psi^\dagger(2')\rangle\right\}\langle S(\infty,-\infty)\rangle^{-1} \tag{A.13}$$

or

$$\left.\frac{\delta G_1(1,1';U)}{\delta U(2'2)}\right|_{U=0} = -G_2(1,2;1',2')+G_1(1,1')G_1(2,2'). \tag{A.14}$$

Several special cases of (A.14) which prove useful can be obtained. By letting $2'\to 2'^+$, i.e., 2 and 2', are at the same time with 2' infinitesimally earlier, one gets the case of the variation of G_1 with respect to a nonlocal one time potential $U(2,2^+)=U(\mathbf{r}_2t_2,\mathbf{r}_2't_2')\delta(t_2-t_2')$

$$\left.\frac{\delta G_1(1,1';U)}{\delta U(2'^+,2)}\right|_{U=0} = -G_2(1,2;1',2'^+)+G_1(1,1')G_1(2,2'^+). \tag{A.15}$$

The special case of the variation of G_1 with respect to a local potential $U(2)$ is obtained from (A.15) by letting $2'\to 2$

$$\left.\frac{\delta G_1(1,1';U)}{\delta U(2)}\right|_{U=0} = -G_2(1,2;1',2^+)+G_1(1,1')G_1(2,2^+). \tag{A.16}$$

For the definition of the functional derivative we note that if F is a functional of $U(x)$ and we change $U(x)$ in the neighborhood of the point x by $\delta U(x)$, then F will change by δF. The limit of $(1/\Delta)[\delta F/\delta U(x)]$ is called the functional derivative (where $\Delta \to 0$ and Δ is the length of the interval). If F can be written in the form

$$F[U(x)] = \int K(x)U(x)\,dx$$

then

$$\delta F = \int_{x_0}^{x_1} K(x')\,\delta U(x')\,dx'$$

where $[x_0, x_1]$ is the interval around x where $\delta U(x')$ is different from zero.

If we write

$$\delta F = (x_1 - x_0)K(\bar{x})\delta U(\bar{x})$$

then

$$\lim \frac{\delta F}{(x_1 - x_0)\delta U(\bar{x})} = K(x).$$

Appendix B

Here Eq. (68) is converted to a closed equation for G_2, with an effective potential W (sometimes called a vertex function) so as to give the usual form of the Bethe–Salpeter equation. Combining Eq. (68) with (65) gives

$$G_2(1, 2; 1', 2') = G_1(1, 1')G_1(2, 2') - G_1(1, 2')G_1(2, 1') + \int d3\,d3'\,d4\,d4' G_1(1, 3)G_1(4, 1')\Xi(34'\,43')R(3'2\,4'2'). \quad \text{(B.1)}$$

Defining W by

$$\int d3'\,d4\,d4' G(4, 1')\Xi(34'43')R(3'24'2') = \int d3'\,d4\,d4' G_1(2, 4)W(343'4')G_2(3', 4', 1, '2') \quad \text{(B.2)}$$

(B.1) becomes

$$G_2(1, 2; 1', 2') = G_1(1, 1')G_1(2, 2') - G_1(1, 2')G_1(2, 1') + \int d3\,d3'\,d4\,d4' G_1(1, 3)G_1(2, 4)W(343'4')G_2(3'4', 1'2') \quad \text{(B.3)}$$

which is the usual form of the Bethe–Salpeter equation. Again the equation is for two dressed particles interacting through an effective potential W which has only the truly two-particle correlations. Experience shows that (B.3) is more convenient for hole-hole or particle-particle processes, while Eq. (68) is more useful for hole-particle processes of the type encountered in this work.

Equation (B.2) can easily be converted into an integral equation for WG_2 which has Ξ as its kernel. Clearly a knowledge of Ξ and R is equivalent to a knowledge of W and G_2.

Appendix C

Here the following integral is evaluated

$$I(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4) = \int_{-\infty}^{\infty} d\varepsilon G_1(\mathbf{r}_1, \mathbf{r}_2; \varepsilon)G_1(\mathbf{r}_3, \mathbf{r}_4; \varepsilon - \varepsilon_s) \quad \text{(C.1)}$$

If Eq. (53b) is inserted into (C.1) with the changes in notation

$$\varphi_n(\omega_n) = \begin{cases} \Gamma_n^{-1/2} f_n(\omega_n) & \text{Re}\,\omega_n > 0 \\ \Gamma_n^{-1/2} g_n(\omega_n) & \text{Re}\,\omega_n < 0 \end{cases} \quad \text{(C.2)}$$

then Eq. (C.1) becomes

$$I = \int d\varepsilon \Bigg\{ \lim_{\eta \to 0+} \sum_{kk'} \frac{f_k(\mathbf{r}_1)\bar{f}_k(\mathbf{r}_2)f_{k'}(\mathbf{r}_3)\bar{f}_{k'}(\mathbf{r}_4)}{(\varepsilon - \varepsilon_k + i\eta)(\varepsilon - \varepsilon_s - \varepsilon_{k'} + i\eta)} + \lim_{\eta \to 0+} \sum_{kl'} \frac{f_k(\mathbf{r}_1)\bar{f}_k(\mathbf{r}_2)g_{l'}(\mathbf{r}_3)\bar{g}_{l'}(\mathbf{r}_4)}{(\varepsilon - \varepsilon_k + i\eta)(\varepsilon - \varepsilon_s - \varepsilon_{l'} - i\eta)} + \lim_{\eta \to 0+} \sum_{lk'} \frac{g_l(\mathbf{r}_1)\bar{g}_l(\mathbf{r}_2)f_{k'}(\mathbf{r}_3)\bar{f}_{k'}(\mathbf{r}_4)}{(\varepsilon - \varepsilon_l - i\eta)(\varepsilon - \varepsilon_s - \varepsilon_{k'} + i\eta)} + \lim_{\eta \to 0+} \sum_{ll'} \frac{g_l(\mathbf{r}_1)\bar{g}_l(\mathbf{r}_2)g_{l'}(\mathbf{r}_3)\bar{g}_{l'}(\mathbf{r}_4)}{(\varepsilon - \varepsilon_l - i\eta)(\varepsilon - \varepsilon_s - \varepsilon_{l'} - i\eta)} \Bigg\}. \quad \text{(C.3)}$$

The first and fourth integrals vanish since both factors in each integral have poles only in the same half plane. If the integration contour is closed in the half plane which does not contain any poles, the residue theorem assures us that the integrals are zero. For the other two integrals, since they have poles in both half planes the contours can be closed either way giving the same result. The second term can be closed in the lower half plane giving

$$\lim_{\eta \to 0+} \int d\varepsilon \frac{F(\varepsilon)}{\varepsilon - \varepsilon_k + i\eta} = -2\pi i \lim_{\eta \to 0+} F(\varepsilon_k - i\eta) = \lim_{\eta \to 0+} \frac{-2\pi i}{\varepsilon_k - \varepsilon_s - \varepsilon_{l'} - i\eta} \quad \text{(C.4)}$$

where the (-1) comes in because the contour is traversed in a clockwise

manner. Similarly closing the contour for the third term in the upper half plane gives

$$\lim_{\eta\to 0+}\int d\varepsilon \frac{1}{(\varepsilon-\varepsilon_l-i\eta)(\varepsilon-\varepsilon_s-\varepsilon_{k'}+i\eta)}=\lim_{\eta\to 0+}\frac{2\pi i}{\varepsilon_l-\varepsilon_s-\varepsilon_{k'}+i\eta}. \tag{C.5}$$

Hence the integral is

$$I(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4)=2\pi i\lim_{\eta\to 0+}\left\{-\sum_{kl'}\frac{f_k(\mathbf{r}_1)\bar{f}_k(\mathbf{r}_2)g_{l'}(\mathbf{r}_3)\bar{g}_{l'}(\mathbf{r}_4)}{\varepsilon_k-\varepsilon_s-\varepsilon_{l'}-i\eta}\right.$$
$$\left.+\sum_{lk'}\frac{g_l(\mathbf{r}_1)\bar{g}_l(\mathbf{r}_2)f_{k'}(\mathbf{r}_3)\bar{f}_{k'}(\mathbf{r}_4)}{\varepsilon_l-\varepsilon_s-\varepsilon_{k'}+i\eta}\right\}. \tag{C.6}$$

REFERENCES

Abrikosov, A. A., Gorkov, L. P., and Dzyaloshinski, I. E. (1963). "Methods of Quantum Field Theory in Statistical Physics." Prentice-Hall, Englewood Cliffs, New Jersey.

Baym, G., and Kadanoff, L. P. (1961). *Phys. Rev.* **124**, 287.

Bell, J. S., and Squires, E. J. (1959). *Phys. Rev. Letters* **3**, 96.

Brout, R., and Carruthers, P. (1963). "Lectures on Many-Electron Problem." Wiley, New York.

Burke, P. H., and McVicar, D. D. (1965). *Proc. Phys. Soc. (London)* **86**, 989.

Csanak, Gy., Taylor, H. S., and Yaris, R. (1971). *Phys. Rev.* **A3**, 1322.

Dalgarno, A., and Victor, G. A., (1966). *Proc. Roy. Soc. Ser. A* **291**, 291.

Dietrich, K., and Hara, K. (1968). *Nucl. Phys. A* **111**, 392.

Dunning, T. H., and McKoy, V. (1967). *J. Chem. Phys.* **47**, 1735.

Dutta, N. C., Ishibara, T., Matsubara, C., Pu, R. T., and Das, T. P. (1969). *Phys. Rev. Letters* **22**, 8.

Dyson, F. J. (1949). *Phys. Rev.* **75**, 486, 1736.

Ehrenreich, H., and Cohen, M. H. (1959). *Phys. Rev.* **115**, 786.

Falkoff, D. (1962). *In* "The Many-Body Problem" (Bergen School Lectures) (C. Fronsdal, ed.). Benjamin, New York.

Fetter, A. L., and Watson, K. M. (1965). *Advan. Theoret. Phys.* **1**, 115–194.

Feynman, R. P. (1948). *Rev. Mod. Phys.* **20**, 367.

Feynman, R. P. (1950). *Phys. Rev.* **80**, 440.

Feynman, R. P. (1951). *Phys. Rev.* **84**, 108.

Galitski, V. M., and Migdal, A. (1958). *Soviet Physics, JETP* **34**(7), 96.

Gell-Mann, M., and Low, F. E. (1951). *Phys. Rev.* **84**, 350.

Goldberger, M. L., and Watson, K. M. (1964). "Collision Theory." Wiley, New York.

Goldstone, J. (1957). *Proc. Roy. Soc. (London) A* **239**, 267.

Goscinski, O., and Lindner, P. (1970). *J. Math. Phys.* **11**, 1313.

Gutfreund, H., and Little, W. A. (1969). *Phys. Rev.* **183**, 68.

Hedin, L., Johansson, A., Lundquist, B. I., Lundquist, S., and Samathiyakamit, V. (1969). *Arkiv. Fysik* **39**, 97.

Jamieson, M. J. (1969). Ph.D. Thesis, The Queen's University of Belfast, Belfast, Northern Ireland.

Janev, R. K., Zivanovic, D. J., and Maric, Z. D (1969). The Use of Green Functions in Electron-Atom Scattering Problem, *In Int. Conf. Phys. Electron. At. Collisions*. M.I.T. Press, Cambridge.

Kadanoff, L. P., and Baym, G. (1962). "Quantum Statistical Mechanics." Benjamin, New York.

Karplus, M., and Caves, T. C. (1969). *J. Chem. Phys.* **50**, 3549.

Kato, T., Kobayashi, T., and Namiki, M., (1960). *Progr. Theoret. Phys. Suppl.* **15**, 3.

Kelly, H. P. (1968). *Advan. Theoret. Phys.* **2**, 75.

Kelly, H. P. (1969). *Phys. Rev.* **182**, 84.

Kirzhnits, D. A. (1967). "Field Theoretical Methods in Many-Body Systems." Pergamon, Oxford.

Klein, A. (1956). *Progr. Theoret. Phys.* **14**, 580.

Klein, A., and Zemach, C. (1957). *Phys. Rev.* **108**, 126.

Layzer, A. J. (1963). *Phys. Rev.* **129**, 897.

Lemmer, R. H., and Veneroni, M. (1968). *Phys. Rev.* **170**, 883.

Linderberg, J. (1968). *Magy. Fiz. Foly.* **16**, 5.

Löwdin, P. O. (1955). *Phys. Rev.* **97**, 1474.

Löwdin, P. O. (1956). *Advan. Phys.* **5**, 1.

March, N. H., Young, W. H., and Sampanthar, S. (1967). "The Many-Body Problem in Quantum Mechanics." Cambridge Univ. Press, Cambridge, England.

Martin, P. C., and Schwinger, J. (1959). *Phys. Rev.* **115**, 1342.

Matsubara, T. (1955). *Progr. Theoret. Phys. (Kyoto)* **14**, 351.

Mattuck, R. D. (1967). "A Guide to Feynman Diagram in the Many-Body Problem." McGraw-Hill, New York.

Migdal, A. B. (1967). "Theory of Finite Fermi Systems." Wiley (Interscience), New York.

Morse, P. M., and Feshbach, H. (1953). "Methods of Theoretical Physics." McGraw-Hill, New York.

Mott, N. F., and Massey, H. S. W. (1965). "The Theory of Atomic Collisions." Clarendon Press, Oxford, England.

Namiki, M. (1960). *Progr. Theoret. Phys.* **23**, 629.

Pines, D., ed. (1961). "The Many-Body Problem." Benjamin, New York.

Pines, D. (1963). "The Many-Body Problem" (D. Pines, ed.). Benjamin, New York.

Reinhardt, W. P., and Doll, J. D. (1969). *J. Chem. Phys.* **50**, 2769.

Reinhardt, W. P., and Szabo, A. (1970). *Phys. Rev.* **A1**, 1162.

Roman, P. (1965). "Advanced Quantum Theory," p. 308. Addison-Wesley, Reading, Massachusetts.

Rowe, D. J. (1968). *Rev. Mod. Phys.* **40**, 153.

Schneider, B. (1970). *Phys. Rev*, **A2**, 1873.

Schneider, B., Taylor, H. S., Yaris, R. (1970). *Phys. Rev.* **1A**, 855.

Schweber, S. S. (1961). "An Introduction to Relativistic Quantum Field Theory." Harper, New York.

Schwinger, J. (1951). *Proc. Nat. Acad. Sci. U.S.* **37**, 452.

Thouless, D. J. (1961). "The Quantum Mechanics of Many-Body Systems." Academic Press, New York.

Wilkinson, J. H. (1965). "The Algebraic Eigenvalue Problem." Clarendon, Oxford, England.

Zmuidzinas, J. S. "Self-consistent Green's Function Approach to the Electron Gas Problem" (preprint).