Eidelsberg, Ann. Astrophys. 22, 614 (1966).

[11] J. M. Robinson and H. B. Gilbody, Proc. Phys. Soc. (London) 92, 589 (1967).

[12] J. H. Moore, Jr., and J. P. Doering, Phys. Rev. 177, 218 (1969).

[13] L. Vegard, E. Tonsberg, and G. Kvite, Geophys. 18, No. 4 (1951).

[14] D. Barbier and D. R. Williams, J. Geophys. Res. 55, 401 (1950).

[15] K. C. Clark and A. E. Belon, J. Atmospheric Terres. Phys. 16, 205 (1959).

[16] L. M. Branscomb, R. J. Shalek, and T. W. Bonner, Trans. Am. Geophys. Union 35, 107 (1954).

[17] B. A. Whalen, I. B. McDiarmid, and E. E. Budzinski, Can. J. Phys. 45, 3247 (1967).

[18] J. T. Park and F. D. Schowengerdt, Rev. Sci. Instr. 40, 753 (1969).

[19] Colutron Corp., Boulder, Colo.

[20] J. T. Park and F. D. Schowengerdt, Phys. Rev. 185, 152 (1969).

[21] M. K. S. Baratron 77M-XRP, M. K. S. Instruments, Inc., Burlington, Mass.

[22] P. M. Stier and C. F. Barnett, Phys. Rev. 103, 896 (1956).

[23] G. Herzberg, Phys. Rev. 69, 362 (1946).

[24] F. R. Gilmore, J. Quant. Spectry. Radiative Transfer 5, 369 (1965).

[25] E. N. Lassettre and M. E. Krasnow, J. Chem. Phys. 40, 1248 (1964).

[26] H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. 44, 355 (1966).

[27] E. N. Lassettre, A. Skerbele, and V. D. Meyer, J. Chem. Phys. 45, 3214 (1966).

[28] Y. Tanaka, J. Opt. Soc. Am. 45, 663 (1955).

[29] V. D. Meyer, A. Skerbele, and E. N. Lassettre, J. Chem. Phys. 43, 3769 (1965).

[30] J. Geiger and W. Stickel, J. Chem. Phys. 43, 4535 (1965).

[31] R. S. Mulliken, in The Threshold of Space, edited by M. Zelikoff (Pergamon Press Inc., New York, 1957).

[32] J. Geiger and B. Schroder, Proceedings of the Fifth International Conference on Physics of Electronic and Atomic Collisions (Nauka Publishing House, Leningrad, 1967), p. 563.

[33] F. J. De Heer, J. Schutten, and H. Moustafa, Physica 32, 1766 (1966).

[34] E. S. Solov'ev, R. N. Il'in, V. A. Oparin, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. 42, 659 (1962) [English transl.: Soviet Phys. – JETP 15, 459 (1962)].

[35] Y. S. Gordeev and M. N. Panov, Zh. Tekhn. Fiz. 34, 857 (1964) [English transl.: Soviet Phys. – Tech. Phys. 9, 656 (1964)].

[36] P. G. Wilkinson, J. Mol. Spectry. 6, 1 (1961).

[37] R. S. Mulliken, Phys. Rev. 57, 500 (1940).

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Many-Body Theory of the Elastic Scattering of Electrons from Atoms and Molecules

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We present a method for calculating the elastic scattering of electrons from atoms and molecules using the many-body Green's-function techniques of Martin and Schwinger. The procedure involves the self-consistent solution of a pair of equations; one for the one-particle Green's function and the other for the response function of the target in the time-dependent Hartree-Fock approximation (random-phase approximation). That both equations are one-dimensional provides a great computational advantage over more conventional techniques. We discuss the physical nature of our approximation and a numerical scheme to implement our theoretical discussion.

I. INTRODUCTION

A. Historical

The problem of the elastic scattering of electrons from atoms and molecules has received considerable attention in the literature in the last few years, and a number of methods have been developed to handle the problem. Temkin[1-4] and Callaway[5] have used the "adiabatic" method to incorporate the distortions of the target by the incoming electron with considerable success for small atomic systems. Quite recently, Callaway[5] has been able to extend the theory to account for some of the effects of the finite kinetic energy of the incoming electron. While these adiabatic or quasiadiabatic methods are quite useful in practical situations, it is not always clear that the approximations involved in their derivation are quantitatively justified.[6] As the incoming electron is drawn into the core by the long-range polarization potential, its kinetic energy becomes comparable to those of the target particles. Under such circumstances, quasiadiabatic methods break down, and one must resort to other techniques to handle the problem.[7] In particular, the back coupling of the target particles to the incoming electron is totally neglected in these theories. In principle, one can eliminate all such problems by using the close-coupling method of Burke and Schey.[8] However, though these methods are capable of yielding as good an answer as one desires, they require the use of large numbers of target states to correctly describe the distortions of the target and become somewhat unwieldy in practice. Two papers in the literature are noteworthy in that they approach the elastic scattering problem from a different point of view, namely, from many-body perturbation theory. As has been shown by Bell and Squires,[9] the self-energy of the one-particle Green's function is formally identical to the optical potential of conventional scattering theory. Both Kelly[10] and Pu and Chang[11] have used this equivalence to do accurate low-energy elastic scattering calculations of electrons from small atoms. In this paper we will show, using the equation-of-motion method of Martin and Schwinger,[12] how one can derive an approximation to the optical potential capable of accurately predicting elastic scattering cross sections. In contrast to the usual perturbation methods, our theory may be viewed as a sort of generalized self-consistent-field (SCF) method in which all approximations are made in the equations of motion. In the course of deriving our working equations, the relationship between scattering theory and the frequency-dependent response function of the target will become apparent. In Sec. IB, we discuss elastic scattering to show what physical effects need to be accounted for in any quantitative theory.

B. Physical Model

An electron incident on an atom or molecule, first and foremost, causes a large distortion of the target wave function. If one considers this in a static picture, such as the Hartree-Fock (HF) model, these distortions are found basically to be the polarization of the target orbitals caused by the electric field of the incoming electron. This can, of course, be described in terms of one-electron excitations from the occupied target orbitals. One can think of the incident electron as moving in the potential of the polarized target. Since the incident electron is moving, the target feels not a static electric field but a field that depends on the incident-electron trajectory. Thus, the polarization of the target is explicitly time-dependent. The time-dependent nature of the polarization potential is reflected in a new path for the incident electron which, in turn, causes a change in the polarization of the target, etc.

The distortion of the target orbitals due to the incident electron changes not only the field in which the external electron moves but also that felt by the target electrons. This is shown by the HF Hamiltonian being a function of the electron density, which has now been changed by the interaction with the incident electron. Allowing for the change in the HF potential caused by the incident electron is called coupled HF theory or in its time-dependent version, the random-phase approximation (RPA) (time-dependent HF).[13-16] The polarization outlined above is known to describe long- and intermediate-range interactions between the incident electron and the target. However, as the incident electron is accelerated by the induced polarizations, shorter-range two-particle correlations between incident and target electrons begin to become significant. Thus the explicit two-particle interactions should be taken into account in order to adequately describe the scattering event. When one properly takes account of the indistinguishability of electrons, improving target-incident-electron correlation automatically improves target-target correlations.

All the physical effects discussed above are naturally incorporated into the Green's-function method of Martin and Schwinger.[12] In brief outline, the scheme we propose involves the self-consistent solution of two basic equations: the equation for the linear-response function of the target and the equation for the one-particle Green's function. The first of these equations, the equation for the linear response function of the target in the RPA, depends on the knowledge of the single-particle Green's function. The second equation, an integrodifferential equation for the Green's function, depends upon a knowledge of the target-response function. Hence, a self-consistent procedure is called for. If one starts by choosing the Green's function as that of the HF model, the equation for the response function becomes the well-known time-dependent coupled HF approximation. This gives the polarization of the target orbitals in the field of the external electron and also the change of the average correlation among these electrons. On the basis of the calculation of frequency-dependent susceptibilities with the time-dependent HF method[16] (which compare very favorably with experimental measurements), and from double-perturbation-theory investigations,[17] one can expect very accurate target polarizations. In evaluating the spectral representation of the response, one obtains a set of poles which are the excitation energies of the target. Having obtained the response function, we now proceed to use that result to solve the one-particle Green's-function equation. In solving for the Green's function, one takes explicit account of the interaction of the polarized target and the incident electron, and also adds further correlation effects to the target. Once we have the solution of the Green's function we return to resolve the response function equation, using the new Green's function as input. We loop these two equations until self-consistency is obtained. When this process is completed, the response function of the target is no longer linear, due to the iteration process.

One obtains the scattering function by solving for the continuum orbitals in the spectral expansion of the one-particle Green's function. That these are in fact the true scattering functions can be seen by examining the equation for the Green's function. For energies in the continuum, this equation becomes the Lippmann-Schwinger equation for the scattering of a particle from the true optical potential. From scattering theory, these continuum orbitals then yield the phase shifts and elastic cross sections.

It is well known from the theory of Green's functions[18] that one may obtain a variety of quantities, such as natural orbitals,[19] ionization potentials, the exact correlation energy[20] of the target, etc., from a knowledge of the one-particle Green's function. It is clear that it would be very difficult to carry out the calculation of the Green's function with a sufficient basis set to obtain all such quantities accurately, even with the most modern techniques. What we shall do is to tailor our basis to accurately describe the response function over most of its energy range. Solving the matrix equations in such a space may well sacrifice other quantities in this work, which concerns itself primarily with scattering.

Below, we will present the Green's function formalism outlined above. This will be followed by a discussion of the physical content of the equations and a suggested numerical method. In Sec. VI, we will point out some of the problems which arise in the solution of these equations and how we may utilize the experience obtained from time-dependent perturbation problems.

II. THEORY

In order to treat all particles equivalently, it is most natural to formulate the problem in terms of the time-dependent second-quantized field operators, ψ and $\psi^\dagger$. These operators, respectively, annihilate and create an electron at position $\vec{r}$ and time t and satisfy the usual Fermion anticommutation relations. In what follows, we will use the notation n to refer to space, spin, and time points. In terms of a complete one-electron basis $\{\varphi_i\}$, we may write

$$\psi(1)=\sum_i c_i(t)\varphi_i(\vec{r}) \ , \tag{2.1a}$$

$$\psi^\dagger(1)=\sum_i c_i^\dagger(t)\varphi_i^*(\vec{r}) \ , \tag{2.1b}$$

where c_i and $c_i^\dagger$ are, respectively, the time-dependent annihilation and creation operators for state i. The field operators satisfy the equation of motion[20]:

$$\left(i\frac{\partial}{\partial t_1}-h_1\right)\psi(1)=\int d2\, V(1-2)\psi^\dagger(2)\psi(2)\psi(1) \ , \tag{2.2}$$

where $$h_1=\frac{p_1^2}{2m}-\frac{Z}{r_1} \ , \tag{2.3a}$$

the bare one-electron Hamiltonian in natural units ($e=\hbar=1$), and

$$V(1-2)=V(\vec{r}_1-\vec{r}_2)\delta(t_1-t_2) \ . \tag{2.3b}$$

In terms of these field operators, one defines the one- and two- particle Green's functions as[20]:

$$G_1(1,1')=(1/i)\langle T[\psi(1)\psi^\dagger(1')]\rangle \ , \tag{2.4a}$$

$$G_2(12,1'2')=(1/i^2)\langle T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]\rangle \ , \tag{2.4b}$$

where T is the well-known time-ordering operator and the angular brackets denote an average over the exact state of the system. For our purposes, this averaging is always over the exact target ground state. We will defer a discussion of the properties of the Green's function until later and turn our attention to the problem of obtaining a tractable set of equations for G_1. By differentiating (2.4a) with respect to t_1 and using (2.2), one obtains after a little manipulation[20]

$$\left(i\frac{\partial}{\partial t_1}-h_1\right)G_1(1,1')+i\int d2\, V(1-2)G_2(12,1'2^+) = \delta(1-1') \ . \tag{2.5}$$

Throughout the paper, we use the convention that $t_2^+=t_2+\delta$, where δ is a positive infinitesimal. One should note that the equation of motion for G_1 is given in terms of G_2. Similarly, the equation for G_2 depends on G_1 and G_3, etc. Written in this form, this hierarchy of coupled equations has the same mathematical structure as the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) equation of statistical mechanics. In order to solve these equations, one must truncate the hierarchy at some point. This is a difficult and dangerous procedure, since one has little physical insight into the effect of such truncations. One can also expand in a perturbation series and then solve the resulting equation for G_1.[18, 20]

In contrast to both of these procedures, Martin and Schwinger have recast the problem in a form much more suitable to physical understanding and approximation, using the method of functional differentiation with respect to an artificial time-dependent external potential. It is not necessary to specify the explicit form of this potential, since, after all functional differentiation has been performed, the external potential is set equal to zero. The fundamental identity of Martin and Schwinger[12] (derived in their paper) is

$$\frac{\delta G_1(1,1')}{\delta U(2)} = -G_2(12,1'2^+) + G_1(1,1')G_1(2,2^+) \ , \tag{2.6}$$

where U is the external potential. Equation (2.6) is now substituted into (2.5) eliminating G_2 in favor of G_1 and its functional derivative.

$$\left(i\frac{\partial}{\partial t_1} - h_1\right)G_1(1,1') + i\int d2\, V(1-2) \times\left(G_1(2,2^+) - \frac{\delta}{\delta U(2)}\right)G_1(1,1') = \delta(1-1') \ . \tag{2.7}$$

For convenience, it is useful to define an auxiliary function[20]:

$$\Sigma(1,1') = -i\int d2\, d3\, V(1-2) \times G_2(12,32^+)G_1^{-1}(3,1') \ , \tag{2.8a}$$

$$\Sigma(1,1') = -i\delta(1-1')\int d2\, V(1-2)G_1(2,2^+) + i\int d2\, d3\, V(1-2)\, \frac{\delta G_1(1,3)}{\delta U(2)}\, G_1^{-1}(3,1'). \tag{2.8b}$$

This function is usually called the self-energy operator and has been shown by Bell and Squires[9] to be the optical potential of scattering theory. Using (2.8a), Eq. (2.5) can be rewritten

$$\left(i\frac{\partial}{\partial t_1} - h_1\, G(1,1') - \int d2\, \Sigma(1,2)G(2,1') = \delta(1-1')\right). \tag{2.9}$$

Since G_2 will no longer appear in any of the equations to follow, we drop the subscript on G_1. It is clear from (2.9) that a knowledge of the self-energy is sufficient to solve for G. We will now use the method of functional differentiation to eliminate the $\delta G/\delta U$ in Eq. (2.7) in favor of $\delta\Sigma/\delta U$. Differentiating the identity

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

yields

$$-\frac{\delta G(1,1')}{\delta U(2)} = \int d3\, d4\, G(1,3)\frac{\delta G^{-1}(3,4)}{\delta U(2)}\, G(4,1') \ . \tag{2.10}$$

In the presence of the external potential

$$G^{-1}(1,1') = G_0{}^{-1}(1,1') - U(1)\delta(1-1') - \Sigma(1,1'), \tag{2.11}$$

where G_0 is the free-particle Green's function. Substituting (2.11) into (2.10) gives

$$\frac{\delta G(1,1')}{\delta U(2)} = G(1,2)G(2,1') + \int d3\, d4\, G(1,3)\, \frac{\delta\Sigma(3,4)}{\delta U(2)}\, G(4,1') \ , \tag{2.12}$$

which on substitution into (2.8b) gives

$$\Sigma(1,1') = -i\delta(1-1')\int d2\, V(1-2) \times G(2,2^+) + iV(1-1')G(1,1'^+) + i\int d2\, d3\, V(1-2)G(1,3)\, \frac{\delta\Sigma(3,1')}{\delta U(2)} \ . \tag{2.13}$$

At this point, it is evident from (2.9) and (2.13) that we must have an expression for $\delta\Sigma/\delta U$ in order to solve for G and Σ. By repeating the procedure of functional differentiation on (2.13) we obtain

$$\frac{\delta\Sigma(1,1')}{\delta U(2)} = -i\delta(1-1')\int d4\, V(1-4)\frac{\delta G(4,4^+)}{\delta U(2)} + iV(1-1')\frac{\delta G(1,1')}{\delta U(2)} + i\int d3\, d4\, V(1-3)\frac{\delta G(1,4)}{\delta U(2)} \times\frac{\delta\Sigma(4,1')}{\delta U(3)} + i\int d3\, d4\, V(1-3)G(1,4)\,\frac{\delta^2\Sigma(4,1')}{\delta U(2)\delta U(4)} \ . \tag{2.14}$$

Noting that (2.12) has eliminated $\delta G/\delta U$ in favor of $\delta\Sigma/\delta U$, and mentally using this in (2.14), it is apparent that one is replacing a hierarchy of Green's-function equations by a similar hierarchy of functional derivatives. In order to close this set of equations, one must still employ a truncation procedure. The advantage of truncating this hierarchy rather than the one in the G's is that one is able to provide a better physical motivation for the truncation procedure. In Sec. III, we shall present the explicit truncation procedure in detail.

Before concluding the section on the general theory, we present several equations which will be used later on. Since it is convenient to work in energy variables, we Fourier transform Eq. (2.9) to yield an expression for the energy-dependent Green's function:

$$[z-h(\vec{r}_1)]G(\vec{r}_1,\vec{r}_1',z) - \int d\vec{r}_2\Sigma(\vec{r}_1,\vec{r}_2,z)G(\vec{r}_2,\vec{r}_1',z)=\delta(\vec{r}_1-\vec{r}_1') \quad , \qquad (2.15)$$

where z has the dimensions of energy and may be complex. It is very useful to have G in diagonal form,[21] that is, its spectral representation. In this representation, G has the form

$$G(\vec{r}_1\vec{r}_1',z)=\sum_n \frac{\phi_n(\vec{r}_1,z)\overline{\phi}_n^{\,*}(\vec{r}_1',z)}{z-E_n(z)} \quad . \qquad (2.16)$$

Since G does not in general satisfy an equation of motion with a Hermitian operator, it cannot be diagonalized by a simple orthogonal set of functions. The functions $\{\phi_n\}$ and $\{\overline{\phi}_n\}$ which diagonalize G and appear in (2.16) form a biorthogonal set and satisfy the eigenvalue equations[21]:

$$h(r_1)\phi_n(\vec{r}_1,z)+\int d\vec{r}_1'\Sigma(\vec{r}_1\vec{r}_1',z)\phi_n(\vec{r}_1,z) = E_n(z)\phi_n(\vec{r}_1,z) \quad , \qquad (2.17\text{a})$$

$$h(r_1)\overline{\phi}_n(\vec{r}_1z)+\int d\vec{r}_1'\,\overline{\phi}_n(\vec{r}_1',z)\,\Sigma^*(\vec{r}_1'\vec{r}_1,z) = E_n^*(z)\overline{\phi}_n(\vec{r}_1,z) \quad . \qquad (2.17\text{b})$$

For values of z below the first excitation threshold, the operator remains Hermitian and the biorthogonal set collapses to the usual orthogonal form. For values of $E_n(z)$ lying in the continuous spectrum, Eq. (2.17a) is equivalent to the Lippmann-Schwinger equation with Σ being the optical potential. Hence, once we have closed our set of equations, we can construct the optical potential and solve for the scattering function and phase shifts by standard scattering techniques.

III. APPROXIMATION SCHEME

In order to obtain a practical approximation scheme, one must start with a soluble initial approximation. For atoms and molecules HF theory presents just such a starting point. With this idea in mind, we may immediately rewrite (2.13) as

$$\Sigma(1,1')=\Sigma_{\mathrm{HF}}(1,1')+i\int d2\,d3\;V(1-2)G(1,3)\,\frac{\delta\Sigma(3,1')}{\delta U(2)} \quad , \qquad (3.1)$$

where $\Sigma_{\mathrm{HF}}(1,1')=-i\delta(1-1')\int d2\;V(1-2)G(2,2^+)+iV(1-1')G(1,1'^+) \quad , \qquad (3.2)$

and is the ordinary HF potential.[20] That this is indeed the case follows from the fact that

$$\rho(\vec{r}_1\,|\,\vec{r}_1')=-iG(1,1'^+) \quad , \qquad (3.3)$$

where $\rho(r_1|\,r_1')$ is the ordinary one-particle density matrix. Equation (3.3) is an immediate consequence of the definition of the Green's function (2.4a). Similarly, it is convenient to separate $\delta\Sigma/\delta U$ in (2.14) into $\delta\Sigma_{\mathrm{HF}}/\delta U$ and a remainder term, where

$$\frac{\delta\Sigma_{\mathrm{HF}}(1,1')}{\delta U(2)}=-i\delta(1-1')\int dx\;V(1-x)\,\frac{\delta G(x,x^+)}{\delta U(2)}+iV(1-1')\,\frac{\delta G(1,1'^+)}{\delta U(2)} \quad . \qquad (3.4)$$

In this paper we will employ the truncation procedure

$$\frac{\delta\Sigma(1,1')}{\delta U(2)}\cong\frac{\delta\Sigma_{\mathrm{HF}}(1,1')}{\delta U(2)} \quad . \qquad (3.5)$$

In terms of Eq. (2.14) this truncation explicitly drops all terms of second order in the variational derivatives. Such terms are expected to be small since they represent a second-order change in a total internal field with respect to an external parameter. Additional motivation for this truncation will be provided below by considering its relationship to the linear response.

Explicitly using (2.12) with $\delta\Sigma/\delta U$ replaced by $\delta\Sigma_{\mathrm{HF}}/\delta U$ in (3.4) and the resulting equation in turn in the equations for Σ, (3.1) and G, (2.9), we obtain the following approximate *closed* set of equations (denoted by the subscript A)

$$\left(i\frac{2}{2t_1}-h_1\right)G_A(1,1')-\int d2\,\Sigma_A(1,2)G_A(2,1')=\delta(1-1')\ , \tag{3.6a}$$

$$\Sigma_A(1,1')=\Sigma_{\mathrm{HF}}(1,1')+i\int d2\,d3\;V(1-2)G_A(1,3)\;\frac{\delta\Sigma_{\mathrm{HF}}(3,1')}{\delta U(2)}\ , \tag{3.6b}$$

$$\frac{\delta\Sigma_{\mathrm{HF}}(1,1')}{\delta U(2)}=-i\delta(1-1')\int dx\;V(1-x)G_A(x,2)G_A(2,x^{\dagger})+iV(1-1')G_A(1,2)G_A(2,1'^{+})-i\delta(1-1')\int dx\,dy\,dz\;V(1-x)$$
$$\times\left(G_A(x,y)G_A(z,x^{+})\;\frac{\delta\Sigma_{\mathrm{HF}}(y,z)}{\delta U(2)}\right)+iV(1-1')\int dx\,dy\;G_A(1,x)G_A(y,1'^{+})\;\frac{\delta\Sigma_{\mathrm{HF}}(x,y)}{\delta U(2)}\ . \tag{3.6c}$$

Equations (3.6) are a set of coupled equations for G_A and $\delta\Sigma_{\mathrm{HF}}/\delta U$ [note that Eq. (3.6b) is purely quadrature]. These equations are the basic equations of our method and should be solved self-consistently. In Sec. IV below we shall present alternative forms of these equations which are perhaps more familiar and amenable to calculation.

IV. ALTERNATIVE FORMS OF THE THEORY

It is apparent from Eq. (3.4) for $\delta\Sigma_{\mathrm{HF}}/\delta U$ that one could present a slightly different form for the above truncation procedure. To this end we may define[20]

$$R(12,1'^{+}2^{+})=i\;\frac{\delta G(1,1'^{+})}{\delta U(2)}\ . \tag{4.1a}$$

The variation of the density matrix with respect to an external potential is called the linear-response function. As will become apparent from the equations below, the linear-response function is no more than the Green's function for the response of the target to an arbitrary time-dependent external potential.[22] It is this feature which motivates our choice of this approximation. Due to our experience with time-dependent problems, we have some physical feeling for the nature of the truncation. We can rewrite (4.1a) as

$$R(12,1'^{+}2^{+})=i\langle T\{[\psi^{\dagger}(1'^{+})\psi(1)][\psi^{\dagger}(2)\psi(2)]\}\rangle \tag{4.1b}$$

where $[\psi^{\dagger}(1'^{+})\psi(1)]=\psi^{\dagger}(1'^{+})\psi(1)-\langle\psi^{\dagger}(1'^{+})\psi(1)\rangle$.

After inserting a complete set of target states between $\psi(1)$ and $\psi^{\dagger}(2)$ and performing a Fourier transform in time we have

$$R(\vec{r}_1\vec{r}_2,\vec{r}_1{}'\,\vec{r}_2,z)=\sum_{w_n}\frac{\langle 0|\psi^{\dagger}(\vec{r}_1{}')\psi(\vec{r}_1)|n\rangle\langle n|\rho(\vec{r}_2)|0\rangle}{w_n-z-i\epsilon}+\sum_{w_n}\frac{\langle 0|\rho(\vec{r}_2)|n\rangle\langle n|\psi^{\dagger}(\vec{r}_1{}')\psi(\vec{r}_1)|0\rangle}{z+w_n-i\epsilon}\ , \tag{4.2}$$

where $\rho(r)=\psi^{\dagger}(r)\psi(r)$,

and $w_n=E_n{}^T-E_0{}^T$.

If one has a knowledge of the exact target ground state, it is possible to convert the problem of the determination of R into a set of differential equations. These equations are just the Green's-function version of the frequency-dependent perturbation equations. To show this it is only necessary to write (4.2) in operator form,

$$R(\vec{r}_1\vec{r}_2,\vec{r}_1{}'\,\vec{r}_2,z)=\langle 0|\psi^{\dagger}(\vec{r}_1{}')\psi(r_1)\times(-z+\mathcal{H}_T-E_0{}^T-i\epsilon)^{-1}Q\rho(\vec{r}_2)|0\rangle+\langle 0|\rho(\vec{r}_2)\times(z+\mathcal{H}_T-E_0{}^T-i\epsilon)^{-1}Q\psi^{\dagger}(\vec{r}_1{}')\psi(\vec{r}_1)|0\rangle\ , \tag{4.3}$$

where $Q=1-|0\rangle\langle 0|$.

It is easily demonstrated that if one knows the solution to the equations[21]

$$(z-\mathcal{H}_T+E_0{}^T)|F\rangle=Q\rho(\vec{r}_2)|0\rangle\ , \tag{4.4a}$$

$$(-z-\mathcal{H}_T+E_0{}^T)|G\rangle=Q\rho(\vec{r}_2)|0\rangle\ , \tag{4.4b}$$

then the determination of the response is just quadrature. Unfortunately, one rarely has the exact target state in practice, and an exact solution of these equations is impossible.

Up to this point we have made no reference to our approximation procedure. In order to make such contact, we need only recall Eq. (3.4), where the linear response appears explicitly. Substituting

(3.4) into (2.12) with the replacement of $\delta\Sigma/\delta U$ by $\delta\Sigma_{\mathrm{HF}}/\delta U$, we obtain, using (4.1a)

$$
\begin{aligned}
R_A(12,1'^+2^+) &= iG_A(1,2)G_A(2,1'^+) \\
&\quad - i\int d3\,d4\,G_A(1,3)[V(3-4)G_A(3,1'^+)R_A(42,4^+2^+)] \\
&\quad + i\int d3\,d4\,G_A(1,3)[V(3-4)G_A(4,1'^+) \\
&\quad \times R_A(32,4^+2^+)]\,,
\end{aligned}
\tag{4.5a}
$$

or its Fourier transform

$$
\begin{aligned}
R_A(\vec{r}_1\vec{r}_2,\vec{r}_1{}'\vec{r}_2,z) &= \frac{i}{2\pi}\,\Big[\int dz'\,G_A(\vec{r}_1\vec{r}_2,z') \\
&\quad \times G_A(\vec{r}_2\vec{r}_1{}',z'-z) \\
&\quad - \int dz'\,d\vec{r}_3\,d\vec{r}_4\,G_A(\vec{r}_1\vec{r}_3,z') \\
&\quad \times G_A(\vec{r}_3\vec{r}_1{}',z'-z)V(\vec{r}_3-\vec{r}_4)R_A(\vec{r}_4\vec{r}_2,\vec{r}_4\vec{r}_2,z) \\
&\quad \times \int dz'\,d\vec{r}_3\,d\vec{r}_4 G_A(\vec{r}_1\vec{r}_3,z')G_A(\vec{r}_4\vec{r}_1{}';z'-z) \\
&\quad \times V(\vec{r}_3-\vec{r}_4)R_A(\vec{r}_3\vec{r}_2,\vec{r}_4\vec{r}_2,z)\Big]\,.
\end{aligned}
\tag{4.5b}
$$

We emphasize once again that we have done nothing more than rewrite our original truncation procedure in terms of R_A. In turn, we may also write

$$
\begin{aligned}
\Sigma_A(1,1') &= \Sigma_{\mathrm{HF}}(1,1') - i\int d2\,d3\;V(1-2) \\
&\quad \times R_A(32,3^+2^+)V(3-1')G_A(1,1') + i\int d2\,d3\;V(1-2) \\
&\quad \times R_A(32,1'^+2^+)V(3-1')G_A(1,3)\;.
\end{aligned}
\tag{4.6}
$$

Equations (4.5) can be shown to be equivalent to the fully coupled time-dependent HF equations[13, 16] if the one-particle Green's function is taken to be G_{HF}. Since we are solving for G_A and Σ_A self-consistently, we actually wind up with the fully renormalized version of these equations. It is this fact that makes this a highly *nonlinear* theory. Unfortunately, we are stuck with the expression "linear response" since it is the accepted terminology. We point out again that this terminology only has meaning in terms of the *exact* target states. We shall continue below with the first iterate to Eqs. (4.5), that is with G_A replaced by G_{HF}, since this approximation shows how the ordinary time-dependent HF equations appear. The general equations which appear in higher-order iterates are not particularly enlightening and have been relegated to the Appendix. After introducing the spectral representation for G_{HF}, we may take matrix elements of Eq. (4.5b) in this basis to yield (suppressing the subscript A for the moment)

$$
\begin{aligned}
R_{ab}{}^{cd} &= \left(\frac{N_a(1-N_c)}{\mathcal{E}_c-\mathcal{E}_a-z-i\epsilon} + \frac{(N_a-1)N_c}{\mathcal{E}_c-\mathcal{E}_a-z+i\epsilon}\right) \\
&\quad \times\left[\delta_{bc}\delta_{ad} - \sum_{\alpha,\beta}\,(V_{ac}{}^{\beta\alpha} - V_{\beta c}{}^{a\alpha})R_{\alpha b}{}^{\beta d}\right]\,,
\end{aligned}
\tag{4.7}
$$

where $N_c = 1 \quad \mathcal{E}_c \in G^<$

$= 0 \quad \mathcal{E}_c \in G^>$

and $\quad \mathcal{E}_i =$ orbital energies

$$V_{ac}{}^{\beta\alpha} = \langle c\alpha|1/r_{12}|a\beta\rangle\,.$$

It would be very convenient at this stage to have a diagonal representation for R.[13] In such a representation

$$R_{ab}{}^{cd} = \sum_{w_n}\,\frac{X_{ac}{}^{n}X^{n*}{}_{db}\,\mathrm{sgn}(w_n)}{w_n - z - i\epsilon\,\mathrm{sgn}(w_n)}\;, \tag{4.8a}$$

$$
\begin{aligned}
\text{where}\quad X_{ac}{}^{n} &= \langle 0|C_a{}^{+}C_c|n\rangle\,,\; w_n > 0 \\
&= \langle n|C_a{}^{+}C_c|0\rangle\,,\; w_n < 0\;.
\end{aligned}
\tag{4.8b}
$$

We obtain this form by inserting Eqs. (2.1) into (4.2) and converting to a sum over both positive and negative excitation energies. Inserting (4.8a) into (4.7), multiplying by $(z-w_n)$, taking the limit as $z\to w_n$, and canceling common factors of X on both sides of the resulting equation gives

$$X_{ac}{}^{n} = \frac{(N_c-N_a)}{(\mathcal{E}_c-\mathcal{E}_a-w_n)}\sum_{\alpha,\beta}\,(V_{ac}{}^{\beta\alpha} - V_{\beta c}{}^{a\alpha})X_{\alpha\beta}{}^{n}\;, \tag{4.9a}$$

or

$$
\begin{aligned}
(\mathcal{E}_c-\mathcal{E}_a-w_n)X_{ac}{}^{n} &= (N_c-N_a)\sum_{\alpha,\beta}\,(V_{ac}{}^{\beta\alpha} - V_{\beta c}{}^{a\alpha})X_{\alpha\beta}{}^{n}\;.
\end{aligned}
\tag{4.9b}
$$

This equation (actually a pair of coupled equations) is the famous RPA eigenvalue equation. The eigenvectors obey a generalized completeness and orthonormality relation of the form[23]

$$\sum_{w_n} X_{ac}{}^{n}\,\mathrm{sgn}(w_n)X^{n*}{}_{db} = (N_a-N_c)\delta_{ad}\delta_{bc}\;, \tag{4.10a}$$

$$\sum_{a,c} X^{n*}{}_{ac}(N_a-N_c)X_{ac}{}^{n} = \mathrm{sgn}(w_n)\delta_{mn}\;. \tag{4.10b}$$

These equations may be cast into a set of *one*-dimensional coupled integrodifferential equations.[16]

In this latter form they are usually called the coupled time-dependent HF equations. Dalgarno[16] and others have used them in this form for the calculation of frequency-dependent polarizabilities with considerable success. One great advantage of the differential equation formulation is that the possibility of variational approximation immediately suggests itself. Alternatively, we may use the matrix form above or attempt a numerical integration. In any case, once we have the response, we may calculate the first iterate to Σ from (4.6).

After a Fourier transform we can write (4.6) as

$$\Sigma_A(\vec{r}_1\vec{r}_1^{\,\prime},z)=\Sigma_{\rm HF}(\vec{r}_1\vec{r}_1^{\,\prime})-\frac{i}{2\pi}\int d\vec{r}_2\,d\vec{r}_3\,dz'\,V(\vec{r}_1-\vec{r}_2)$$

$$\times[R_A(\vec{r}_3\vec{r}_2,\vec{r}_3\vec{r}_2,z')V(\vec{r}_3-\vec{r}_1^{\,\prime})G_{\rm HF}(\vec{r}_1\vec{r}_1^{\,\prime},z-z')]$$

$$+\frac{i}{2\pi}\int d\vec{r}_2\,d\vec{r}_3\,dz'\,V(\vec{r}_1-\vec{r}_2)[R_A(\vec{r}_3\vec{r}_2,\vec{r}_1^{\,\prime}\vec{r}_2,z')$$

$$\times V(\vec{r}_3-\vec{r}_1^{\,\prime})G_{\rm HF}(\vec{r}_1\vec{r}_3,z-z')]\ . \qquad (4.11\text{a})$$

By substituting the first iterate for R_A, Eq. (4.8a), into (4.11a) and performing the indicated integrations, we obtain

$$\Sigma_A(\vec{r}_1\vec{r}_1^{\,\prime},z)=\Sigma_{\rm HF}(\vec{r}_1,\vec{r}_1^{\,\prime})+\sum_{w_n>0}\ \sum_{\alpha\in G>}\ \sum_{abcd}\frac{V_{bd}(\vec{r}_1)V_{ac}(\vec{r}_1^{\,\prime})X^{n}_{ac}X^{n*}_{db}\varphi_\alpha(\vec{r}_1)\varphi^*_\alpha(\vec{r}_1^{\,\prime})}{z-\mathcal{E}_\alpha-w_n+i\epsilon}$$

$$+\sum_{w_n<0}\ \sum_{\alpha\in G^<}\ \sum_{abcd}\frac{V_{bd}(\vec{r}_1)V_{\alpha c}(\vec{r}_1^{\,\prime})X^{n}_{ac}X^{n*}_{db}\varphi_\alpha(\vec{r}_1)\varphi^*_\alpha(\vec{r}_1^{\,\prime})}{z-\mathcal{E}_\alpha-w_n-i\epsilon}$$

$$-\sum_{w_n>0}\ \sum_{\alpha\in G^>}\ \sum_{abcd}\frac{V_{bd}(\vec{r}_1)V_{\alpha c}(\vec{r}_1^{\,\prime})X^{n}_{ac}X^{n*}_{db}\varphi_\alpha(\vec{r}_1)\varphi^*_a(\vec{r}_1^{\,\prime})}{z-\mathcal{E}_\alpha-w_n+i\epsilon}$$

$$-\sum_{w_n<0}\ \sum_{\alpha\in G^<}\ \sum_{abcd}\frac{V_{bd}(\vec{r}_1)V_{\alpha c}(\vec{r}_1^{\,\prime})X^{n}_{ac}X^{n*}_{db}\varphi_\alpha(\vec{r}_1)\varphi^*_a(\vec{r}_1^{\,\prime})}{z-\mathcal{E}_\alpha-w_n-i\epsilon}\ , \qquad (4.11\text{b})$$

where $V_{ab}(\vec{r}_x)=\int d\vec{r}_y\,\varphi^*_a(\vec{r}_y)\,\frac{1}{\vec{r}_{xy}}\,\varphi_b(\vec{r}_y)$.

We now substitute this result back into Eq. (3.6a) and solve for the orbitals which diagonalize G. Having done this, we use these new orbitals as the driving force in the RPA equations and resolve them. This procedure is continued until the orbitals in the Green's-function equation do not change (self-consistency has been reached). The entire procedure is summarized in the following. (i) Use the HF one-particle Green's function as your initial approximation to G. (ii) Using the time-dependent coupled HF equations [(4.7)–(4.10)] with the original HF orbitals, we solve for the response function. (iii) Using the results of (i) and (ii), we calculate the optical potential [Eq. (4.11)] by quadrature. (iv) Using Σ from (iii), we diagonalize the Green's function, [Eq. (2.17)]. (v) Return to (ii) and use the new orbitals to calculate the response. Repeat the entire procedure until self-consistent.

One should note that at no stage of the calculation do we have to solve more than a *one-particle* equation. In view of the fact that we have a complicated set of coupled equations to solve, this can be an enormous computational saving. In Secs. V and VI we will show exactly what terms we have included in our theory and a numerical scheme to implement our results.

V. DISCUSSION

The physical content of our equations may be understood quite readily by considering the incoming electron as a time- (or frequency-) dependent perturbation of the target electrons. Each frequency component of the incoming wave packet acts as a probe and induces correlations in and among the target electrons. The type of correlations included can be found by an examination of the coupled HF equations. Using our equation for the response, we write these terms using field diagrams (see Fig. 1). All time orderings are implied in this representation. These diagrams can easily be transformed to the more usual Goldstone diagrams, such as appear in the recent paper of Karplus and Caves[17] on the coupled HF method, by realizing that G is a "free" propagator and including all possible time orderings consistent with instantaneous interactions. If one does so, one sees that all of the terms represent particle-hole interaction in the target. Single excitations and a large class of double excitations of the occupied HF orbitals are accounted for. Physically, we expect this to be the

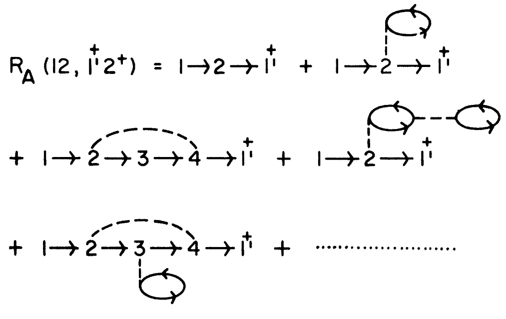

FIG. 1. Solid lines represent one-particle Green's functions; and dotted lines, the interaction potential.

dominant type of correlation neglected in the HF approximation. This, however, is only the target side of the problem. Once we have calculated these polarizations and induced correlations, we must still solve the one-particle Green's-function equation. The solution of this part of the problem is equivalent to the back reaction of the polarization on *all* the particles of the system and the *explicit* introduction of two- and higher-body correlations. Both the target electrons and the incident electron move and interact in a polarized fluctuation potential. As is typical of all Green's-function techniques, we have included some effects to infinite order in the perturbation potential, while we have neglected others entirely. One of the nicer features of the Green's-function method is that it is quite easy to see what terms have been omitted. We need only look at the leading terms of Eq. (2.14) beyond $\delta\Sigma_{\mathrm{HF}}/\delta U$. If we replace G by G_{HF} and $\delta\Sigma/\delta U$ by $\delta\Sigma_{\mathrm{HF}}/\delta U$ on the right-hand side of (2.14), the lowest-order terms are as shown in Fig. 2.

The first two diagrams are of the particle-hole type and represent higher-order polarization and consistency effects within the target. Since we have already accounted for the more important diagrams of this type within the RPA, we do not expect these to contribute significantly. The last two contain hole-hole and particle-particle interaction and, therefore, represent true short-range two-particle correlations of the target. These latter diagrams can easily be taken into account by perturbation theory if it is necessary. It is doubtful that they play a really important role in low-energy elastic scattering for the following reason. As a rule of thumb based on excellent physical and mathematical arguments, the Feynman diagrams, which are important for ordinary optical susceptibilities, are also important for low-energy elastic scattering. The time-dependent HF equations have been shown to give excellent frequency-dependent moments. If one couples this with our additional SCF calculation of the Green's function, which brings in additional correlation, one feels he has accounted for most of the physics outlined in Sec. II. One avoids the explicit solution of a two-particle problem by solving two one-particle equations, one linear in the interaction potential, the other quadratic. By performing the required convolution integral we get a significant fraction of the two-particle correlation with all renormalizations included. The residual two-particle terms which have been neglected are given by Eq. (5.2) to lowest order. By the arguments given above, we expect these to be small in comparison to $\delta\Sigma_{\mathrm{HF}}/\delta U$. We hope to support our conclusions by explicit calculations in a later publication.

VI. NUMERICAL PROCEDURE

The fact that the response function is merely the Green's function for a time- or frequency-dependent perturbation problem allows us to use approximation techniques and insights developed for time-dependent problems.[24] It is of course clear that if one has the exact linear response, one can immediately solve for any frequency-dependent susceptibility exactly. Similarly, if one knows the RPA solution, one knows the susceptibility in the time-dependent HF approximation. The RPA has been known to give excellent results for one-electron perturbations. Within the subspace defined by the target particles $1/r_{12}$ is a one-electron perturbation and, consequently, we expect to get quite reasonable results. Since we know that we are after the response of the target to $1/r_{12}$ type interaction from the structure of the self-energy operator, we try to use a basis for solution which reflects this fact.

In attempting a solution of the RPA equations in a finite basis set, we are immediately faced with the problem of having a finite pole approximation to the response function. This, of course, means that the response function cannot mirror the exact response for all frequencies. This is not a serious problem since the response function goes into a convolution integral. What it does mean is that the

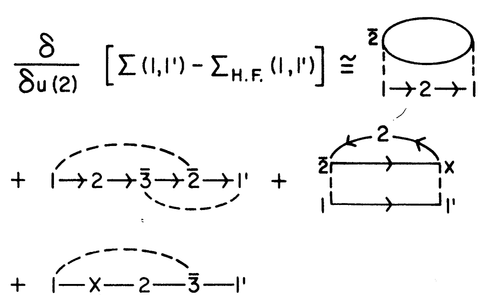

FIG. 2. First two diagrams are of the particle-hole type and represent higher-order polarization and consistency effects within the target; the last two contain hole-hole and particle-particle interaction.

n poles of the approximate response cannot be the same as the first n poles of the exact function, but, in fact, are n effective poles, i.e., the best n poles over the entire frequency range. This is much the same as the use of n pole frequency-dependent polarizabilities to convolute in order to obtain the London dispersion force.

The second problem we must face is what finite one-electron basis set to use. The objective is obviously to obtain a good response to the $1/r_{12}$ interaction with as small a basis as possible. A guide to our thinking is the fact that at large distances $1/r_{12}$ can be expanded in a multipole series. The effect on the target, therefore, is much the same as that observed in the calculation of the various frequency-dependent polarizabilities. It has been shown that a particularly convenient set for these types of calculations can be constructed by using the unperturbed orbitals times a polynomial in radial coordinates with coefficients to be determined by the calculation times the desired spherical harmonic. These basis sets have been shown to be quickly converging for polarizability calculations. The various spherical harmonics, of course, block-diagonalize in the RPA eigenvalue problem, thus keeping the requisite matrix equations small. The number of spherical harmonics which must be included will necessarily await the actual calculation. However, we do not anticipate the need of including a large number of them.

It is apparent from Eq. (4.11a) for the optical potential that the one-particle Green's function is just the other side of the system's response to the $1/r_{12}$ potential. Thus, the physical considerations considered above with respect to the response function apply to the solution of the Green's function problem as well. From such arguments it is apparent that the same form of one-electron basis functions used for the RPA solution would be appropriate for the Green's-function equation. However, one can do even better. Since the RPA solutions have much of the physical effect of the distortions built into them, it is reasonable to use them as our starting point in building up the basis set. One then improves these by multiplying them by a small polynomial in radial coordinates to allow for additional flexibility. As before we have only a small matrix equation to be iterated. Similarly, we can start off the second iteration through the linear response equation with the orbital calculation to the Green's function, again allowing for improvement with a small polynomial. This method of iterating the basis set allows for the incorporation of most of the physics with only small matrix equations at each stage. This should allow for considerable computational savings.

Because of the finite pole approximation it is somewhat difficult to obtain the scattering orbital from the Green's-function equation. This can be easily remedied by solving for the scattering orbital numerically. That is, after one has self-consistency in the Green's-function equation in the finite basis set, one uses the fixed self-energy operator to determine the scattering orbital by numerical integration. This may be done by a noniterative method similar in spirit to the one used by Marriott.[25] By examining the asymptotic behavior of these orbitals, it is a simple task to evaluate the phase shifts. In addition, this can be used as a test of self-consistency by evaluating the phase shifts numerically after each loop through the Green's-function equation. The calculation would be stopped when the phase shifts have stabilized to constant values.

VII. CONCLUSIONS

In this paper, we have described a method for the calculation of elastic scattering of electrons from a many-body system. The method involves the self-consistent solution of the response function of the target in the RPA and the one-particle Green's function. We have discussed the physical motivation for this procedure, described the physical nature of the terms included and the lowest-order correction to our results. We have outlined a possible approach to the numerical solution of these equations which incorporate the physical insights gained from time-dependent perturbation calculations.

It is clear from an examination of the equations we have presented that varying degrees of approximation are possible. The lowest-order approximation would use the RPA response function and the HF Green's function to construct an optical potential which would be used to calculate the scattering function directly. This neglects the short-range effects of correlation on the polarization potential and self-consistency effects within the single-particle Green's function. This is already a good deal better than many of the quasiadiabatic approximations. An intermediate level of approximation would use the RPA response function and solve the integrodifferential equation for the Green's function. Using this Green's function and the RPA response function, we calculate a new optical potential and then solve for the scattering function. This leaves out the explicit effects of correlation on the target polarization. We are going to undertake calculations using this method to investigate the importance of these various effects.

In the absence of calculations, one can already see that a number of theoretical questions have been formally answered. We have seen how to use time-dependent methods in scattering calculations. Specifically, we see how the RPA occurs quite naturally as a lowest-order approximation and how we may incorporate the effects of correlation through the solution of the one-particle Green's function. By making this connection between scattering theory and time-dependent perturbation methods used in susceptibility calculations, we may draw on a wider field of experience. In closing, we would like to point out again that through the use of modern many-body techniques, the intrinsic many-particle equations of scattering theory have been reduced to a set of coupled one-particle equations. One need hardly emphasize the practical simplification this affords.

ACKNOWLEDGMENTS

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APPENDIX: DERIVATION OF THE GENERAL FORM OF EQ. (4.9)

By inserting a complete set of $(N+1)$ and $(N-1)$ particle states in the definition of the Green's function, Eq. (2.4a), we may write

$$G(\vec{r}_1, \vec{r}_1{}', z) = \sum_k \frac{f_k(\vec{r}_1) f_k^*(\vec{r}_1{}')}{z - \mathcal{E}_k + i\epsilon} + \sum_l \frac{g_l(\vec{r}_1) g_l^*(\vec{r}_1{}')}{z - \mathcal{E}_l - i\epsilon} \tag{A1}$$

$$\begin{aligned} &\text{where} \quad \text{(a)} \quad f_k(r_1) = \langle 0 | \psi(\vec{r}_1) | k_{N+1} \rangle, \qquad \text{(b)} \quad g_l(r_1) = \langle l_{N-1} | \psi(\vec{r}_1) | 0 \rangle \\ &\text{and} \quad \text{(c)} \quad \epsilon_k = E_k^{N+1} - E_0, \qquad \text{(d)} \quad \epsilon_l = E_0 - E_l^{N-1} . \end{aligned} \tag{A2}$$

Substituting (A1) into (4.5b) and performing the contour integration yields

$$\begin{aligned} R_A(\vec{r}_1\vec{r}_2, \vec{r}_1{}'\vec{r}_2, z) = \sum_{q,q'} \Bigg(& \frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_q^*(\vec{r}_2)\varphi_{q'}(\vec{r}_2)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_{q'} - z - i\epsilon} \\ & + \frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_q^*(\vec{r}_2)\varphi_{q'}(\vec{r}_2)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_{q'} - z + i\epsilon} \Bigg) - \sum_{q_1 q'} \Bigg(\frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_q{}' - z - i\epsilon} \\ & \times \int d\vec{r}_4 \, V_{qq'}(\vec{r}_4) R_A(\vec{r}_4\vec{r}_2, \vec{r}_4\vec{r}_2, z) + \frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_{q'} - z + i\epsilon} \\ & \times \int d\vec{r}_4 V_{qq'}(\vec{r}_4) R_A(\vec{r}_4\vec{r}_2, \vec{r}_4\vec{r}_2, z) \Bigg) \\ & + \sum_{q,q'} \Bigg(\frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_{q'} - z - i\epsilon} \int d\vec{r}_3 d\vec{r}_4 \, \varphi_{q'}^*(\vec{r}_3) V(\vec{r}_3 - \vec{r}_4)\varphi_{q'}(\vec{r}_4) R_A(\vec{r}_3, \vec{r}_2, \vec{r}_4\vec{r}_2, z) \\ & + \frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q - \mathcal{E}_{q'} - z + i\epsilon} \int \mathrm{d}\vec{r}_3 \, d\vec{r}_4 \, \varphi_q^*(\vec{r}_3) V(\vec{r}_3 - \vec{r}_4)\varphi_{q'}(\vec{r}_4) R_A(\vec{r}_3\vec{r}_2, \vec{r}_4\vec{r}_2, z) \Bigg), \end{aligned} \tag{A3}$$

where we have used the symbol φ_q to represent either f_k or g_l and

$$N_q = 1, \quad \mathcal{E}_q \in G^< \tag{A4a}$$

$$N_q = 0, \quad \mathcal{E}_q \in G^> \tag{A4b}$$

$$V_{qq'}(x) = \int d\vec{y} \, \varphi_q^*(\vec{y}) V(\vec{x} - \vec{y}) \varphi_{q'}(\vec{y}) . \tag{A4c}$$

We now introduce the spectral expansion for R_A into Eq. (A3)

$$R_A(\vec{r}_1\vec{r}_2,\vec{r}_1{}'\vec{r}_2,z)=\sum_{w_n}\frac{\operatorname{sgn}(w_n)x^n(\vec{r}_1{}',\vec{r}_1)x^{n*}(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}\quad, \tag{A5}$$

where $x^n(\vec{r}_1{}',\vec{r}_1)=\langle 0|\psi^{+}(\vec{r}_1{}')\psi(\vec{r}_1)|n\rangle,\quad w_n>0$ (A6a)

$$=\langle n|\psi^{+}(\vec{r}_1{}')\psi(\vec{r}_1)|0\rangle,\quad w_n<0\ . \tag{A6b}$$

to yield

$$\sum_{w_n}\frac{\operatorname{sgn}(w_n)X^n(\vec{r}_1{}',\vec{r}_1)X^{n*}(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}=\sum_{q,q'}\left(\frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_q^*(\vec{r}_2)\varphi_{q'}(\vec{r}_2)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z-i\epsilon}\right.$$

$$\left.+\frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_q^*(\vec{r}_2)\varphi_{q'}(\vec{r}_2)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z+i\epsilon}\right)$$

$$-\sum_{q,q_1'w_n}\left(\frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z-i\epsilon}\ \frac{\operatorname{sgn}(w_n)X^n(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}\int d\vec{r}_4\,V_{qq'}(\vec{r}_4)X^n(\vec{r}_4,\vec{r}_4)\right.$$

$$\left.+\frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z+i\epsilon}\ \frac{\operatorname{sgn}(w_n)X^{n*}(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}\int d\vec{r}_4\,V_{qq'}(\vec{r}_4)X^n(\vec{r}_4,\vec{r}_4)\right)$$

$$+\sum_{q_1q_1'w_n}\left(\frac{N_{q'}(1-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z-i\epsilon}\ \frac{\operatorname{sgn}(w_n)X^{n*}(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}\int d\vec{r}_3\,d\vec{r}_4\,\varphi_q^*(\vec{r}_3)V(\vec{r}_3-\vec{r}_4)\varphi_{q'}(\vec{r}_4)X^n(\vec{r}_4,\vec{r}_3)\right.$$

$$\left.+\frac{N_q(N_{q'}-1)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-z+i\epsilon}\ \frac{\operatorname{sgn}(w_n)X^{n*}(\vec{r}_2,\vec{r}_2)}{w_n-z-i\epsilon\operatorname{sgn}(w_n)}\int d\vec{r}_3\,d\vec{r}_4\,\varphi_q^*(\vec{r}_3)V(\vec{r}_3-\vec{r}_4)\varphi_{q'}(\vec{r}_4,\vec{r}_3)X^n(\vec{r}_4,\vec{r}_3)\right). \tag{A7}$$

We now multiply (A7) by (w_n-z), take the limit as $z\to w_n$, and cancel common factors to get

$$X^n(\vec{r}_1{}',\mathrm{r}_1)=-\sum_{q,q'}\frac{(N_{q'}-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-w_n}\int d\vec{r}_4\,V_{qq'}(\vec{r}_4)X^n(\vec{r}_4,\vec{r}_4)$$

$$+\sum_{q,q'}\frac{(N_{q'}-N_q)\varphi_q(\vec{r}_1)\varphi_{q'}^*(\vec{r}_1{}')}{\mathcal{E}_q-\mathcal{E}_{q'}-w_n}\int d\vec{r}_3 d\vec{r}_4\varphi_q^*(\vec{r}_3)V(\vec{r}_3-\vec{r}_4)\varphi_{q'}(\vec{r}_4)X^n(\vec{r}_4,\vec{r}_3)\ .$$

which is the general form of Eq. (4.9).

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[1] A. Temkin, Phys. Rev. 107, 1004 (1957).

[2] A. Temkin, Phys. Rev. 116, 358 (1959).

[3] A. Temkin and J. C. Lamkin, Phys. Rev. 121, 788 (1961).

[4] A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967).

[5] R. W. La Bahn and J. Callaway, Phys. Rev. 180, 91 (1969) and references cited therein.

[6] M. Mittleman, in Advances in Theoretical Physics, edited by K. A. Brueckner (Academic Press Inc., New York, 1965).

[7] J. Tully, Phys. Rev. 181, 7 (1969).

[8] P. G. Burke and H. M. Schey, Phys. Rev. 126, 147 (1962).

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

[10] H. P. Kelly, Phys. Rev. 160, 44 (1967).

[11] R. T. Pu and E. Chang, Phys. Rev. 151, 31 (1966).

[12] P. C. Martin and J. S. Schwinger, Phys. Rev. 115, 1342 (1959).

[13] M. A. Ball and A. D. McLachlan, Rev. Mod. Phys. 36, 844 (1964).

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

[15] R. A. Harris, J. Chem. Phys. 47, 3972 (1967).

[16] G. A. Victor and A. Dalgarno, Proc. Roy. Soc. (London) 291, 291 (1966).

[17] M. Karplus and T. C. Caves, J. Chem. Phys. 50, 3649 (1969).

[18] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963).

[19] W. Reinhardt and J. Doll, J. Chem. Phys. 50, 2767 (1969).

[20] Leo P. Kadanoff and Gordon Baym, Quantum Statistical Mechanics (W. A. Benjamin, Inc., New York, 1962).

[21] A. J. Layzer, Phys. Rev. 129, 897 (1963).

[22] R. Yaris, J. Chem. Phys. 39, 2479 (1963); 40, 667 (1964); 43, 3528 (1965).

[23] D. J. Thouless, Nucl. Phys. 22, 78 (1961).

[24] P. Sitz and R. Yaris, J. Chem. Phys. 49, 3546 (1968).

[25] R. Marriott, Proc. Roy. Soc. (London) 72, 121 (1958).