A variational principle is proposed for direct calculation of the excitation energy. The spectrum of collective excitations is derived for a homogeneous electron gas.

The poles of the two-particle Green's function in the particle-hole channel are used in the field formulation of the many-body problem to define the single excitations (one-particle and collective). This method has been applied to the excitations of homogeneous electron gas and to the excitation spectra of molecules with conjugated bonds. An attempt has been made [1-6] to calculate the excitations of a multielectron atom via a quasi-homogeneous model.

The Green's function method has the advantages that it readily yields the various expansions in perturbation theory and also allows relations such as Dyson's equations to be written. This is especially simple for a spatially homogeneous system, where the form of the final solution is readily envisaged. Serious difficulties are encountered in this approach for an inhomogeneous bounded system.

Here we show that the Green's-functions formalism is related to a method [7] based on the traditional transition-matrix formalism of quantum chemistry. A variational principle is proposed for determining the excitation spectrum. The method is applied to the collective branch of the excitations in a model for a homogeneous electron gas.

1. Derivation of the Basic Equation

Consider the equation for the poles of the two-particle Green's function:

$$G^{(2)}(x_1, x_2; x'_1, x'_2) = \left( \frac{1}{T} \right)^{\frac{1}{2}} \langle T \left( \Psi(x_1) \Psi^+(x'_1) \Psi(x_2) \Psi^+(x'_2) \right) \rangle$$

in the variables $x_1, x_2, x'_1, x'_2$, in which $x$ includes the spatial and spin coordinates. In the first approximation for the interaction for the vertex part [1]:

$$G^{(2)}(x_1, x_1') + i \int G^{(1)}(x_1, x_2) G^{(1)}(x_2, x_1') V(x_2) \times$$
$$\times G^{(2)}(x_2, x_2') dx_2 dx_3 dt_2 = i \int G^{(1)}(x_1, x_2) G^{(1)}(x_2, x_1') \times$$
$$\times V(x_2, x_2') G^{(2)}(x_2, x_2') dx_2 dx_3 dt_2 = 0,$$  \hspace{1cm} (1)

in which $G^{(1)}(x_1, x_1') = G^{(1)}(x_1, x_2, x_1', x_2'), G^{(1)}(x_1, x_1')$ is the exact one-particle Green's function and $t_2^- = t_2 + \hbar, \hbar = 1$.

We replace $G^{(1)}(x_1, x_1')$ by the one-particle Green's function in the Hartree-Fock approximation, which satisfies in the first and second arguments the equations:

$$\left\{ i \frac{\partial}{\partial t_1} - H_{\text{HF}}(x_1) \right\} G^{(1)\text{HF}}(x_1, x_1') = \delta^2(x_1 - x_1') \delta(t_1 - t'_1),$$

$$\left\{ -i \frac{\partial}{\partial t'_1} - H_{\text{HF}}^*(x_1) \right\} G^{(1)\text{HF}}(x_1, x_1') = \delta^2(x_1 - x_1') \delta(t_1 - t'_1).$$  \hspace{1cm} (2)

From (1) and (2) we have
\[ \left( i \frac{\partial}{\partial t} - H^{\text{HF}}(x_i) \right) G^{(3)}(x_i; x_i', x_i'') + iG^{(0)HF}(x_i; x_i'; x_i'') \times \right] \\
\times \int [V(x_i, x_j) G^{(2)}(x_i', x_i''), dx_j - i \int G^{(1)}(x_i; x_i', x_i'') V(x_i, x_j) G^{(2)}(x_i; x_i', x_i') dx_j = 0; \] (3)

\[ \left( -i \frac{\partial}{\partial t} - H^{\text{HF}}(x_i) \right) G^{(3)}(x_i; x_i', x_i'') + iG^{(0)HF}(x_i; x_i'; x_i'') \times \right] \\
\times \int [V(x_i, x_j) G^{(2)}(x_i', x_i''), dx_j - i \int G^{(1)HF}(x_i; x_i', x_i'') \times \right] \\
\times V(x_i, x_j) G^{(2)}(x_i', x_i'') dx_j = 0. \] (4)

We subtract (4) from (3) and pass to the limit \( t_1 \to t_1 + 0 \) to get the following equation for the Fourier components of \( G^{(2)}(x_i, x_i'; \Delta \epsilon) \)

\[ [h^{\text{HF}}(x_i) - h^{\text{HF}'}(x_i)] G^{(3)}(x_i; x_i', x_i'; \Delta \epsilon) + P(x_i, x_i') \int (V(x_i, x_j) - \int P(x_0, x_0) V(x_i, x_j) G^{(3)}(x_0, x_0, \Delta \epsilon) + \int P(x_i, x_j) V(x_i, x_j) G^{(2)}(x_i, x_i', \Delta \epsilon) = \Delta \epsilon G^{(2)}(x_i, x_i', \Delta \epsilon), \] (5)

in which

\[ G^{(0)HF}(x_i; x_i', x_i'') = - \frac{1}{\beta} \sum_{m=1}^{N} \chi_m(x_i) \chi_m^*(x_i') = P(x_i, x_i'). \]

\[ h^{\text{HF}}(x_i) \chi_m(x_i) = e_m \chi_m(x_i). \]

Now (5) becomes (17) of [7] if we note that \( P(x_i, x_i') = \delta(x_i, x_i') \), so these approximations are obviously equivalent.

2. VARIATIONAL PRINCIPLE

It is convenient to introduce the orthoprojectors

\[ P(x_i, x_i'), \quad R(x_i, x_i') = \delta(x_i, x_i') - P(x_i, x_i'); \]

\[ \int P(x_i, x_i') P(x_i, x_j) dx_i' = P(x_i, x_j), \]

\[ \int R(x_i, x_i') R(x_i, x_j) dx_i' = R(x_i, x_j), \]

\[ \int P(x_i, x_i') R(x_i, x_j) dx_j = 0. \] (6)

We also introduce the operators

\[ v_\pm (x_i, x_i'; x_j, x_j') = P(x_i, x_j) R(x_j', x_i') \pm R(x_j, x_j) P(x_i', x_i). \] (7)

It is readily verified that

\[ \int v_\pm (x_i, x_i'; x_j, x_j') v_\pm (x_i, x_i'; x_j', x_j') dx_j dx_j' = v_\pm (x_i, x_i'; x_j, x_j'), \] (8)

\[ \int v_\pm (x_i, x_i'; x_j, x_j') v_\pm (x_i, x_i'; x_j', x_j') dx_j dx_j' = v_\pm (x_i, x_i'; x_j, x_j'), \] (9)

\[ v_\pm (x_i, x_i'; x_j, x_j') = P(x_i, x_j) \delta(x_j', x_i') - \delta(x_j, x_j) P(x_i', x_i), \]

\[ [h^{\text{HF}}(x_i) - h^{\text{HF}'}(x_i), v_\pm] = 0. \] (11)

It follows from (1) that

\[ v_\pm G^{(2)} = G^{(2)}. \] (12)

This confirms the conclusions of section 2 of [7] as to the general form for the solution to (5), which may be rewritten